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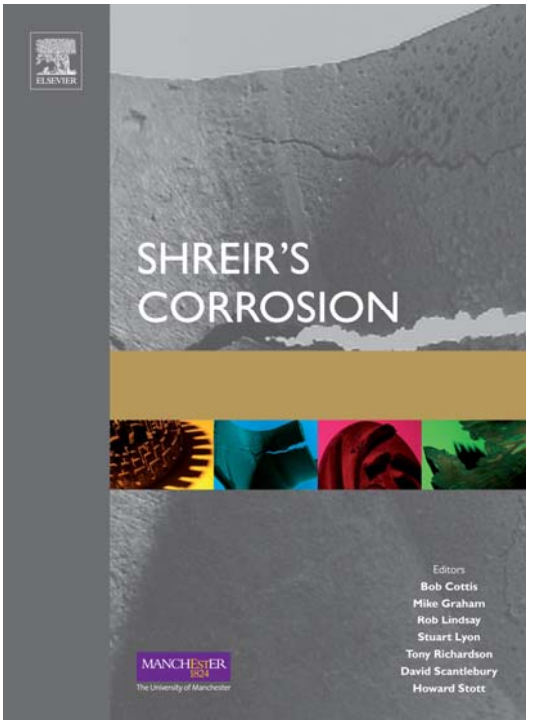

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3.33 Degradation of Natural Rubber and Synthetic Elastomers

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Glossary

Damping Basic property of an elastomer to dampen, absorb or reduce vibrations. High damping elastomers are those having high glass-transition temperature (T_g), which are widely used to isolate vibrations.

Glass-transition temperature (T_g) It denotes the temperature below which the elastomer becomes glassy and brittle, above which it is soft and rubbery. T_g reflects molecular mobility and hence the internal viscosity of the elastomer. High T_g indicates low molecular mobility or high internal viscosity and vice versa.

Heat build-up The amount of heat accumulated in the elastomer when subject to cyclic deformation. It is closely related to hysteresis.

Hysteresis It is a term to denote energy dissipated as heat when the elastomer is subject to cyclic stresses or in a single stress–strain cycle. The area bounded by the extension and retraction curve gives a quantitative measure of hysteresis.

Raw rubber Fresh rubber or an elastomer as received from the supplier.

Scorch It is a rubber technology term to denote the occurrence of a premature crosslink, which is an undesirable feature during the shaping process.

Vulcanizate or vulcanized elastomer Indicates rubber or elastomer that has been vulcanized or cured, and thus, contains network structure or chemical crosslinks.

Abbreviations

ACM Polyacrylic rubber
ASTM American Society for Testing Materials
CED Cohesive energy density
CIIR Chlorinated butyl rubber
CM Cement metal failure
CP Cement primer failure
CR Polychloroprene rubber
CSM Chlorosulfonated polyethylene rubber
DCP Dicumyl peroxide
DOPPD Dioctyl-*p*-phenylenediamines
ECO Copolymer of epichlorohydrin rubber
ENR50 Epoxidized natural rubber (50 mol% epoxidation)
EPM Ethylene propylene rubber
EV Efficient vulcanization
GRG General rubber goods
IHRD International Rubber Hardness Degrees
IIR Isobutylene isoprene (butyl) rubber
IR Synthetic polyisoprene rubber
IRG Industrial rubber goods
ISO International Organization for Standardization
MRB Malaysian Rubber Board
MRPRA Malaysian Rubber Producers Research Association
MS Malaysian standard
NBR Nitrile rubber
NR Natural rubber
PP Polypropylene
PTR Polysulphide rubber
SBR Styrene butadiene rubber
TAC Triallyl cyanurate
TAIC Triallylisosyanurate
TARRC Tun Abdul Razak Research Centre
UiTM Mara University of Technology
UV Ultraviolet light
XNBR Carboxylated nitrile rubber

Symbols

A Cross-sectional area (m^2)
***A*$_o$** Unstrained (original) cross-sectional area (m^2)
B Crack growth constant
c Crack length (mm, m)
***c*$_o$** Natural flaw size (mm, m)
***C*$_o$** Concentration of antiozonant ($mg\,cm^{-2}$)

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C_s Concentration of antiozonant at the rubber surface (mg cm^{-2})
D Diffusion coefficient ($m^2\,s^{-1}$)
dc/dt Crack growth rate ($m\,s^{-1}$)
f Force (N)
f_f Frequency (Hz)
h Height (m)
k_c Compression stiffness ($N\,m^{-1}$)
k_s Shear stiffness ($N\,m^{-1}$)
l Half thickness of film sheet (mm, m)
L Length (m)
M Molecular weight ($g\,mol^{-1}$)
M_∞ Total mass of liquid absorbed after an infinite time (g, kg)
M_L Mass of layer per unit area of surface ($g\,mm^{-2}$, $kg\,m^{-2}$)
M_t Total amount of liquid absorbed per unit area after immersion time, t ($g\,mm^{-2}\,s^{1/2}$)
N Number of molecules per unit volume of rubber ($mol\,cm^{-3}$)
N_f Fatigue life (number of cycles of failure) (cycles, kilocycles)
R Molar gas constant (8314 $J\,mol^{-1}\,K^{-1}$)
S Shape factor
T Absolute temperature (K)
t Time (s)
T_g Glass-transition temperature (°C, K)
V_1 Molar volume of solvent (m^3)
v_f Volume fraction of seeding particles present in the rubber
v_r Volume fraction of rubber in the swollen gel
W Width (m)
W_s Strain energy density ($J\,m^{-3}$)
$[X]_{phy.}$ Physically manifested crosslink concentration ($mol\,kg^{-1}$)
δ Solubility parameter $(MPa)^{1/2}$
ΔH Latent heat of vaporization (J)
λ Extension ratio
ρ Density ($kg\,m^{-3}$)
χ Rubber–solvent interaction parameter

3.33.1 Introduction

Natural rubber and elastomers belong to the same group of materials known as high molecular weight polymers. According to the International Organization for Standardization (ISO) rubber vocabulary,[1] an elastomer is a macromolecular material which returns rapidly to approximately its initial dimensions and shape after substantial deformation by a weak stress and release of the stress. However, an elastomer has always been recognized as a synthetic elastic polymer.[1] A polymer is a high molecular weight material having many units of small molecules chemically joined or linked by normal covalent bonds to form long chain molecules. These flexible and soft materials find wide uses in many engineering applications, such as natural rubber (NR) bridge bearings, and earthquake and seismic bearings. Indeed NR has had a sound track record in many engineering applications for over 150 years.[2] Elastomers have some unique properties that metals do not have. These include

- high bulk modulus (2000–3000 MPa) relative to their Young's modulus (0.5–3.0 MPa),
- some inherent damping, and
- large strain deformation.

Rubbers having high bulk modulus hardly change their volume when deformed. In simple words, rubber is incompressible. Like incompressible liquids, it has a Poisson's ratio close to 0.5. If rubber is constrained, to prevent changes in shape, it becomes much stiffer, a feature that is used to full advantage in the design of compression springs. Elastomeric bridge bearings and seismic bearings are examples of products that rely on these properties.

The damping inherent in the elastomer is a very important property as it helps to prevent the amplitude of the vibration of the spring from becoming excessive if resonant frequencies are encountered. Elastomeric products such as vibration isolators and engine mounts rely on the inherent damping properties of the elastomer.

The elastomer undergoes large strain deformation (a few hundred percent) without failure by an applied stress below its breaking stress. This means that it can store much more energy per unit volume than steel. Elastomeric dock fender systems make use of its large stored energy capacity to absorb shocks, blows and the impact exerted by ships.

Some of the merits of elastomeric springs over metal springs are as follows[2]:

- no maintenance is required,
- the energy storage capacity is high,
- with correct design, the rubber spring can provide different stiffness in different directions, or nonlinear load–deflection characteristics,
- a certain amount of misalignment is tolerable as the rubber spring can accommodate this tolerance,
- easier to install,
- hysteresis inherited by the elastomer is able to dampen dangerous resonant vibrations.

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Another important property of an elastomer is its strong resistance to inorganic acids, salts, and alkalis. In contrast, acids attack metals. For these reasons, the linings of chemical tanks and pipes, especially those containing caustic solutions, are made from elastomers. The function of the elastomer here is to protect the metal against attack by corrosive chemicals.

Every product has its own life span. The designed lifetime of a product depends on the environmental conditions and the nature of the application. It is very important to choose the materials correctly to meet the intended service conditions and the surrounding environment. The aging process is the determining factor that limits the life span of the product. The term aging is always associated with the degradation or corrosion process as applied to metals, which may take many forms. In metals, corrosion takes place in the form of rusting, which involves oxygen and moisture. In elastomers, the term degradation is preferred to corrosion and covers a wider scope than that of metals. Degradation takes place in the form of oxidation, ozone cracking, flex cracking, liquid absorption and heat aging. Degradation in elastomers is very complex as it involves oxygen, ozone, mechanical strain, heat, trace metals, etc. There are other agencies such as solvents, oils, fuels, hot air (steam) and water, which may degrade elastomers and affect the service life of elastomeric products. A specific section on the degradation of elastomers discusses all these issues again later.

3.33.2 Classifications of Rubber and Elastomers

3.33.2.1 Classification in Terms of Origins

Natural rubber comes from trees known as *Hevea brasiliensis*, and shrubs called guayule. The pictures in **Figure 1** show typical rubber trees grown in the hot tropical climate of Malaysia, and the fresh latex that exudes from the bark of the rubber tree, after tapping with a sharp tapping knife. The fresh latex that exudes from the tree known as field latex contains about 70% water. After removing this large amount of unwanted water, the latex is known as concentrated latex and has about 60% of rubber content. Centrifuging is the preferred method of concentrating field latex because of its efficiency and rapidness compared to creaming and evaporation methods. Apart from latex, natural rubbers are available commercially in standard bale form, weighing about 33.33 kg. These bales of NR are produced specifically to meet certain technical requirements such as minimum dirt content, viscosity consistency, ash content, etc.

Figure 1 Pictures of (a) natural rubber trees (top), (b) NR latex exudes from natural rubber tree (middle), and (c) closer view of NR latex collected in a cup (bottom).

All synthetic elastomers are produced by the polymerization process. The early production of synthetic elastomers such as styrene butadiene rubber (SBR), polychloroprene rubber (CR), and nitrile rubber (NBR) relied on emulsion polymerization. One of the main drawbacks of emulsion polymerization is the lack of uniformity of polymer molecules with respect to stereo regularity. This is due to the

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different ways in which diene monomer molecules can react, and it applies to all free radical polymerization processes of diene monomers. However, there was a real breakthrough with the discovery of the Ziegler–Natta catalyst in 1954, which enabled the control of the microstructure of polyisoprene.[3] Synthetic polyisoprene is produced by the solution polymerization process using catalysts of the alkyl lithium types such as trialkyl aluminum/titanium tetrachloride mixtures.[3] The Al/Ti mole ratio is critical for achieving high cis content. Currently, there are about 27 types of rubbers or more commercially available in the market. The choice depends on the nature of application, service conditions and environment.

3.33.2.2 Classification in Terms of Purposes

Elastomers can be classified further either as general-purpose rubbers or as specialty rubbers. General-purpose rubbers are those elastomers that are widely used in the manufacture of tires, industrial rubber goods (IRG), and general rubber goods (GRG). Most of the general-purpose elastomers cannot meet high service temperature and high oil resistance specifications or the combinations of these two requirements. The most common general-purpose rubbers include NR, SBR, CR, NBR, ethylene–propylene–diene rubber (EPDM), and BR. In contrast, specialty rubbers are those elastomers that are tailor made to meet certain specific requirements, such as low temperature flexibility, high swelling resistance towards oil (hydrocarbon, fuel, gasoline, etc.) and very high service temperature or combinations of these requirements. Specialty rubbers include silicone rubber, fluoroleastomers, epicholorohydrin, cholorosulfonated rubber, etc. **Table 1** shows some of the rubbers which belong to these grades and their typical applications.

3.33.2.3 Classification in Accordance with International Organization for Standardization

Elastomers can also be classified according to the ISO 4632/1-1982(E)[4] which provides information about rubber as a material with specifications. They are classified and designated in terms of their performance to heat aging, swelling resistance towards oil and low temperature flexibility. This method of classification is very helpful as it facilitates the purchasers and suppliers to make the correct selection of suitable materials, and avoid wasting time and energy.

These designations are determined by a type based on resistance to heat aging, by a class based on resistance to swelling in oil, and by a group based on low temperature resistance.[4] These classification criteria are used to establish a characteristic material designation consisting of three capital letters, where

- the first letter signifies Type (heat resistance)
- the second letter signifies Class (oil resistance)
- the third letter signifies Group (low temperature resistance).

Tables 2–4 show the heat aging temperature, limits of volume swell and brittleness temperature for establishing Type, Class and Group respectively.[4] Type is determined by the maximum temperature at which heat (air oven) aging for 70 h, in accordance with ISO 188, causes a change in tensile strength of not more than ±30%, a change in elongation at break of not more than −50%, and a change in hardness of not more than ±15 International Rubber Hardness Degrees (IHRD). Class is based on the resistance of the material to swelling in American Society for Testing Materials (ASTM) Oil No. 3, when tested in accordance with ISO 1817. In the test, the immersion time shall be 70 h at a temperature determined in **Table 2**. Group is based on the brittleness temperature of the material when measured in accordance with ISO/R 812.

Thus if an elastomer is designated as BCD, it means that it is classified as Type B, Class C and Group D. This implies that the elastomer resists temperatures up to 100 °C, with volume swelling not exceeding 120% in oil No. 3 and is not brittle at −40 °C.

Most of the general purpose elastomers shown in **Table 1** have poor heat resistance except for ethylene propylene rubber (EPM) as shown in **Figure 2**. EPM can withstand service temperature of about 150 °C as it is categorized as Type D. General purpose elastomers also have poor swelling resistance towards hydrocarbon oil except nitrile rubber (NBR) which is classified as Class H with maximum volume swell of 30%. A majority of the specialty elastomers shown in **Table 1** have both excellent heat resistance and swelling resistance. From the chart shown in **Figure 2**, silicone rubber having both methyl and vinyl substituent groups on the polymer chain (VMQ) has equivalent heat resistant (Type G) with silicone rubber having methyl, vinyl, and fluorine substituent groups on the polymer chain (FVMQ). However, they have different Class with respect to swelling resistance. VMQ belongs to Class E while FVMQ belongs to Class J. Clearly

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Table 1 General purpose rubbers and specialty rubbers

General purpose rubbers	*Typical applications*	*Specialty rubbers*	*Typical applications*
Natural rubber (NR)	Mainly for tires, industrial and general rubber goods, bridge and earthquake bearings, bridge expansion joints, etc.	Carboxylated nitrile rubber (XNBR)	Oil resistant hoses, boots, seals and gaskets and other automotive components with very good oxidation resistance
Synthetic polyisoprene (IR)	Tires, sports goods, earthquake rubber bearings, IRG.	Polysulphide rubber (PTR)	Used mainly where good resistance to solvents is required
Styrene butadiene rubber (SBR)	Passenger car tires, IRG, GRG	Polyurethane rubber (AU, EU)	Gaskets, seals, solid tires, and foams
Butyl rubber (IIR)	Tire tubes, tube liners, enclosures, air bags, and curing bladders	Silicone rubber (Si)	Able to withstand a very wide range of service temperatures from −45 to 200 °C. Various grades are available covering a very wide range of applications such as baby teats, catheters, medical applications, wire and cables, electronic components, etc.
Butadiene rubber (BR)	Tires, sports goods	Chlorosulfonated polyethylene rubber (CSM)	Electrical insulator in cable and wire industry, tank lining, colored-stable weather-resistance products, oil resistant hoses and gaskets
Ethylene–propylene–diene rubber (EPDM)	Gaskets, seals, automotive components, IRG, and GRG	Polyacrylic rubber (ACM)	Seals and gaskets for high temperature applications, 180–200 °C
Polychloroprene rubber (CR)	Hoses, rubber bearings, expansion joints, belts, and conveyors	Fluorocarbon rubber (FPM)	Products which are resistant to chemicals, oils and solvents. Able to withstand high service temperatures exceeding 250 °C. Outstanding oxidation and ozone resistance. Flame resistant. Hoses, gaskets and seals for aircraft, jets, and rockets
Nitrile rubber (NBR)	Oil-resistant hoses, seals, O-rings, gaskets	Epichlorohydrin rubber (ECO)	Automotive industry – gasket, seals, hoses to withstand service temperatures above 130 °C

Table 2 Heat aging temperature for establishing Type[4]

	Type									
	A	B	C	D	E	F	G	H	J	K
Test temperature (°C)	70	100	125	150	175	200	225	250	275	300

Table 3 Limits of volume swelling for establishing Class[4]

	Class										
	A	B	C	D	E	F	G	H	J	K	L
Vol. swell max. (%)	No rqmt.	140	120	100	80	60	40	30	20	10	5

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Table 4 Limiting brittleness temperatures for establishing Group[4]

	Group						
	A	B	C	D	E	F	G
Limiting brittleness temperature (°C)	0	−10	−25	−40	−55	−75	−85

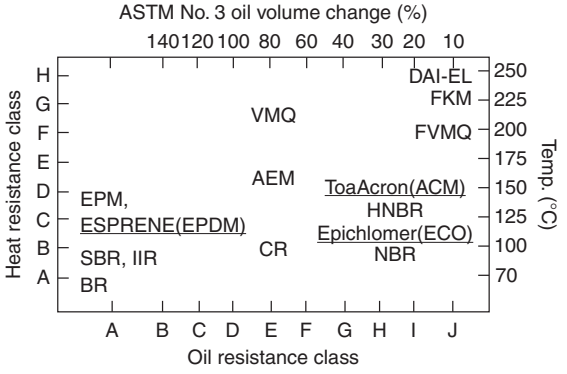

Figure 2 A chart showing type and class of elastomers. Adapted from Hashimoto, K.; Maeda, A.; Hosoya, K.; Todani, Y. *Rubb. Chem. Technol.* **1998,** *70*(3), 449–519, with permission from American Chemical Society.

FVMQ is more resistant to swelling towards the solvent than VMQ grade, as the fluorine atom is highly polar. Figure 3 shows the general chemical structure of silicone rubber with different substituent groups.

The main backbone chain is made of repeating −Si−O− groups while the methyl groups are attached at the side. Both Si–O and Si–CH_3 bonds are thermally stable. This explains why VMQ and FVMQ grades have the same Type of heat resistance, as the main chain backbone is the same for both. The Si–O bond is partially ionic and it is relatively easy to be broken by concentrated acids and alkalis even at room temperature. Another important feature of the chemical structure of silicone rubber is the relatively large bond angle of Si–O (about 140–160°).[7] The intermolecular forces between silicone chains are very low probably because of the large distance between the adjacent chains, as silicone atoms are relatively large. Thus this facilitates ease of chain rotation which accounts for the lowest glass-transition temperature T_g (∼−120 °C) among the commercially available elastomers. The dimethyl rubbers swell more in aliphatic and aromatic hydrocarbons than in acetone and diesters. However, the swelling resistance towards hydrocarbon oil can be enhanced by the replacement of one methyl group on each silicon atom by a more polar group such as trifluropropyl group ($-CH_2CH_2CF_3$), that is, the FVMQ grade.

3.33.3 General Properties of Elastomers

All elastomers have some common properties such as being flexible, tough, relatively impermeable to both water and air, and elastic when vulcanized. One of the unique features of a vulcanized elastomer is its ability to exhibit high elasticity: the elastomer can be stretched to a few hundred percent and recover its original shape and dimensions almost instantaneously when the deforming force is released. For a material to exhibit high elasticity, it must fulfill the following conditions:

- flexible long chain molecules with relatively low molecular interaction forces,
- the long chain molecules must be cross linked (at least 2% cross linked network),
- rubbery above T_g.

The elasticity of an ordinary solid such as metal is associated with its internal energy. In contrast, the elasticity of rubber is entropy driven.

Elastomers are also well known for their good resistance to acids, alkali and chemical solutions. Elastomers have a proven record of accomplishment as the material used for tank lining or related chemical vessels. Beyond these common characteristics, each rubber has its own unique properties depending on the chemical structure as discussed briefly below.

3.33.3.1 Structure–Property Relationship

The effects of chemical structure on some important physical and technological properties are summarized in Table 5.

3.33.3.1.1 Mechanical strength

Tensile strength, tear strength, crack-growth resistance and fatigue life of the vulcanized elastomer depend on the chemical structure and its geometrical configurations. Elastomers having regular microstructure are able to crystallize, and those that have irregular microstructure are amorphous. Figure 4 shows the chemical structure of general-purpose elastomers such

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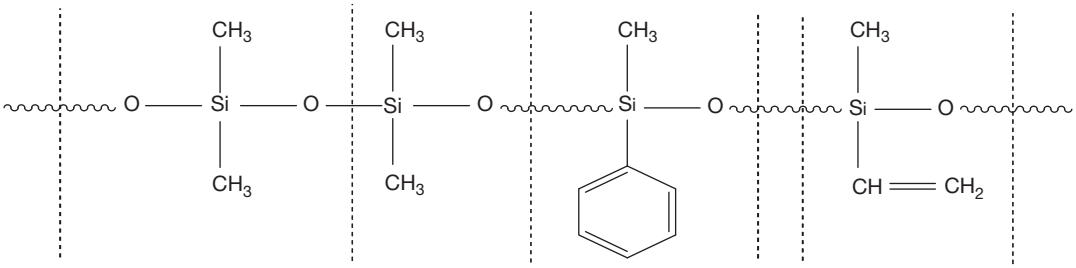

Figure 3 Chemical structure of silicone rubber: MQ grade consists of methyl, PMQ grade consists of benzene rings and VMQ grade consists of vinyl.

Table 5 Influence of chemical structure on physical and technological properties of elastomers

Basic structure	*Technological significance*
1. Nature of carbon–carbon backbone chain (i) Double bonds (ii) Single bonds	Unsaturated elastomers (having double bonds) are capable of being vulcanized with sulfur. Saturated elastomers (having single bonds) cannot be vulcanized with sulfur, but with peroxide. Unsaturated elastomers have poorer ozone cracking resistance and poorer oxidative resistance than saturated elastomers
2. Geometrical configurations	Regular microstructure would favor crystallization. Irregular microstructure leads to amorphous elastomers. The degree of crystallization affects mechanical strength
3. Polarity	Affects the degree of swelling resistance, rubber to metal bond strength, T_g and electrical resistivity
4. Chain flexibility and glass transition temperature, T_g	Affects hysteresis and damping, and other related properties such as resilience, heat build-up, mechanical strengths, etc.
5. Molecular weight distribution	Broad molecular weight distribution provides easier processing than narrow molecular weight distribution

as natural rubber (NR), styrene butadiene rubber (SBR) and polychloroprene rubber (CR).

Natural rubber is 100% *cis*-1,4-polyisoprene indicating that it has regular microstructure, thus enabling it to crystallize. NR will crystallize at low temperatures. Crystallization has its own kinetic; in the case of NR the maximum rate of crystallization occurs at −26 °C.[2,6] When the rubber crystallizes, it hardens progressively and eventually loses its flexibility and rubber-like elasticity. The maximum amount of crystalline region is about 33% in the case of NR. However, if a tensile strain (more than 200%) is applied to NR it crystallizes almost instantaneously even at high temperatures. This phenomenon is known as strain-induced crystallization. Since crystallization is a reversible process, the crystals are completely melted once the applied strain is removed.

Low temperature crystallization brings few disadvantages to NR, particularly when it involves mixing. When NR crystallizes, it becomes very stiff and may cause damage to the mills. To overcome this problem, the common practice is to place the crystallized NR in a hot room (oven) to melt the crystals so that the rubber regains its flexibility. Any unmelted crystals present during the mixing process would interfere with the incorporation and dispersion of the compounding ingredients. In contrast, strain-induced crystallization offers a big advantage in that it helps to enhance the mechanical strength of the rubber. For example, an unfilled or gum NR vulcanizate gives higher tensile strength (23–27 MPa) than unfilled SBR gum vulcanizate (2–3 MPa). Unfilled (gum) vulcanizate refers to a vulcanized rubber containing no filler apart from the compounding ingredients necessary for vulcanization. The crystals that are formed during straining act like a reinforcing filler to enhance the tensile strength. Thus for a noncrystallizing elastomer, it is necessary to incorporate a reinforcing filler into the rubber to enhance its strength.

In addition to the reinforcing filler, the types of chemical crosslink such as polysulfidic(C–S_x–C), monosulfidic (C–S–C), or carbon–carbon (C–C) also affect the strength of the vulcanized elastomer.[8] Polysulfidic crosslinks are weak and labile with lower bond energy than monosulfidic and carbon–carbon links. Polysulfidic crosslinks enhance mechanical strengths such as tensile and tear strengths because these weak and labile crosslinks relieve stresses by 'yielding.'[8]

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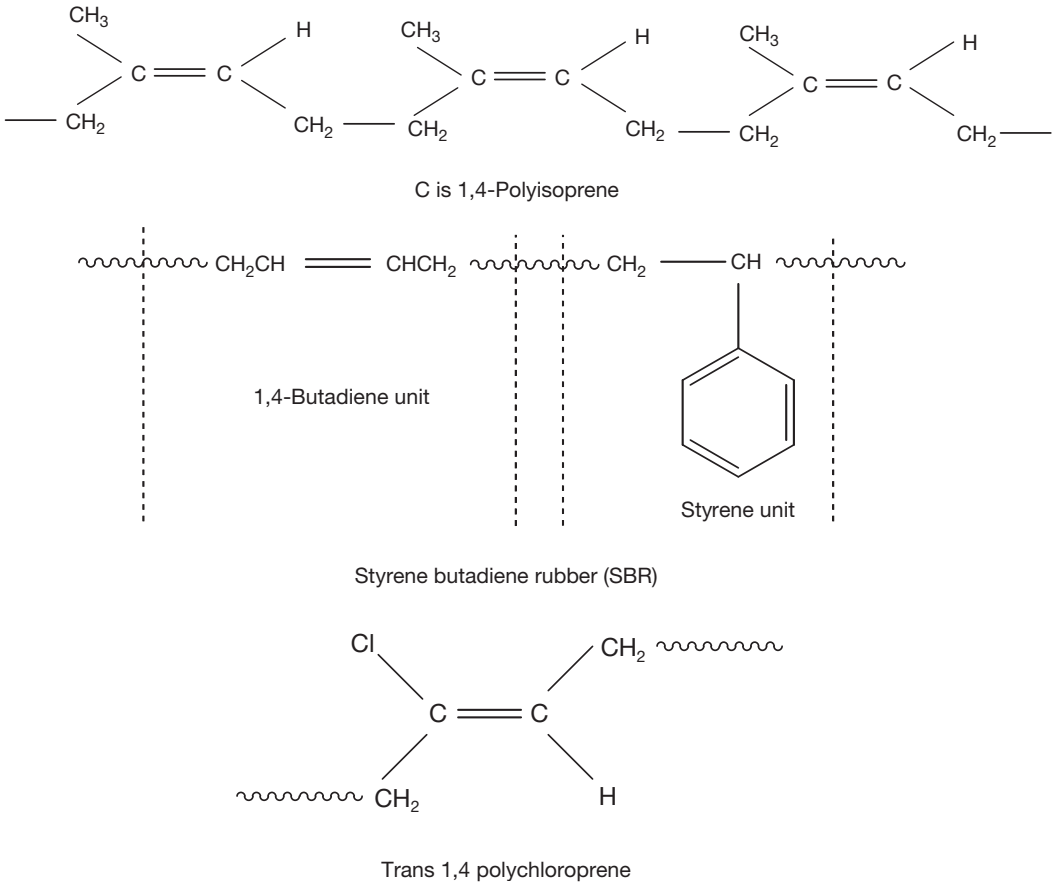

Figure 4 Chemical structure of general-purpose elastomers.

Besides NR, polychloroprene rubber (CR) can also crystallize. Indeed CR crystallizes more readily than NR does because trans 1,4 configuration allows better molecular packing than cis 1,4 configuration.

3.33.3.1.2 Oxidation and ozone resistance

All unsaturated elastomers are susceptible to attack by oxygen and ozone which ultimately leads to chain scission followed by progressive loss in the physical properties. This aspect of oxidation will be discussed further in a later section. Almost all specialty elastomers have saturated bonds on the main backbone as well as high bond dissociation energy. Thus, specialty elastomers are highly resistance to heat, oxidation and ozone cracking.

3.33.3.1.3 Swelling resistance

The swelling resistance of rubber towards hydrocarbon oil depends on the extent of the polarity of the elastomer. The more the polar groups attached to the rubber molecules the higher is the polarity, and the better is the swelling resistance towards hydrocarbon oil. The solubility parameter of elastomers and liquids determines the extent of compatibility and swelling resistance. The closer the solubility parameters between the elastomer and the liquid, the better is their compatibility. Indeed, the greater the thermodynamic compatibility between liquid and elastomer, the greater the absorption of liquid occurring when both have similar solubility parameters. The solubility parameter δ is related to a parameter to measure the specific interaction between molecules known as cohesive energy density (CED) by the following mathematical relationship.

$$\delta = (\mathrm{CED})^{1/2} \quad [1]$$

$$\mathrm{CED} = (\Delta H - RT)/(M/\rho) \quad [2]$$

where ΔH is the latent heat of vaporization, T is the absolute temperature, M is the molecular weight of the polymer, ρ is the density of the polymer, and R is the molar gas constant. For example, natural rubber has a solubility parameter value of 16.7 and NBR has

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a solubility parameter between 21.0 and 22.0 $MPa^{1/2}$. Most of the petroleum oils have a solubility parameter of 16.3 $MPa^{1/2}$. Thus NR will swell markedly in petroleum oil because their solubility parameters are similar. In contrast, NBR has a solubility parameter very much higher than that of petroleum oil, so the two are not compatible. For this reason, polar NBR shows higher swelling resistance than nonpolar NR towards petroleum oil. Elastomers with higher polarity such as polyurethane rubber (AU) show even higher swelling resistance to nonpolar solvents than nonpolar elastomers. Based on the solubility parameter, polar rubbers swell more in polar solvents. Nonpolar rubbers are resistant to swelling in polar solvents.

3.33.3.1.4 Glass-transition temperature T_g

The glass-transition temperature (T_g) is the temperature at which molecular mobility begins to take place, below which molecular mobility is frozen and the elastomer becomes rigid and glassy. The T_g of the elastomer depends on the chemical structure of the elastomer. The presence of a polar atom, side groups, length of side chains, and crosslink reduces molecular mobility which would increase T_g of the elastomer. The glass-transition temperature affects a number of important technological properties such as strength, damping, low temperature flexibility, rolling resistance, wet grip, etc. High T_g elastomers are preferred to low T_g elastomers for applications where high mechanical strength, high damping, and excellent wet traction are required. For applications where excellent low temperature flexibility, low heat generation, high resilience and low rolling resistance are required, low T_g elastomers are preferred to high T_g elastomers.

Table 6 summarizes the respective T_g, ozone cracking resistance, chemical resistance and heat aging resistance of some of the important commercial elastomers.

3.33.4 Rubber Technology and Compounding

3.33.4.1 Mastication and Mixing

Rubbers find very limited applications in their raw form. In their raw form, rubbers may be suitably used as binders and adhesives because of their inherent tack. To become useful products, they have to undergo various processes from mastication, mixing, shaping or fabrication prior to molding, as shown by the schematic flow chart in Figure 5.

3.33.4.2 Rubber Compounding

Rubber compounding is the term used to denote the art and science of selecting and combining elastomers and additives to obtain an intimate mixture that will develop the necessary physical and chemical properties for a finished product. In compounding, one must cope with literally hundreds of variables in materials and equipment. There are three main areas of concern in rubber compounding, namely, (i) to secure certain properties in the finished product to

Table 6 Some important technological properties of some important commercial elastomers

Elastomer	*T_g (°C)*	*O_3 resistance*	*Swelling resistance (%)[a]*	*Heat resistant up to (°C)[b]*
NR	−72	L	200 (120 °C)	100
SBR	−63	L	130 (120 °C)	100
BR	−112	L	>140 (70 °C)	100
EPDM	−55	H	>140 (70 °C)	150
IIR	−66	M	120 (120 °C)	150
CIIR	−66	M	>140 (150 °C)	150
ACM	−22 to −40	H	25 (150 °C)	175
CO	−26	H	5 (150 °C)	150
CR	−45	M	65 (120 °C)	125
NBR (med ACN)	−34	L	10 (100 °C)	125
MVQ	−120	VH	50 (150 °C)	225
CSM	−25	H	50 (150 °C)	150
H-NBR	−30	H	15 (150 °C)	150
FKM	−18 to −50	VH	2 (150 °C)	250
EU	−55	H	40 (100 °C)	100

[a]Swelling after 70 h in ASTM oil 3.[5,9]
[b]Classification after ISO/TR 8461, aerobic condition, Method ISO 4632/1 3 days, (Retention properties).[9]
L = low resistance M = medium resistance H = high resistance.[5,9]

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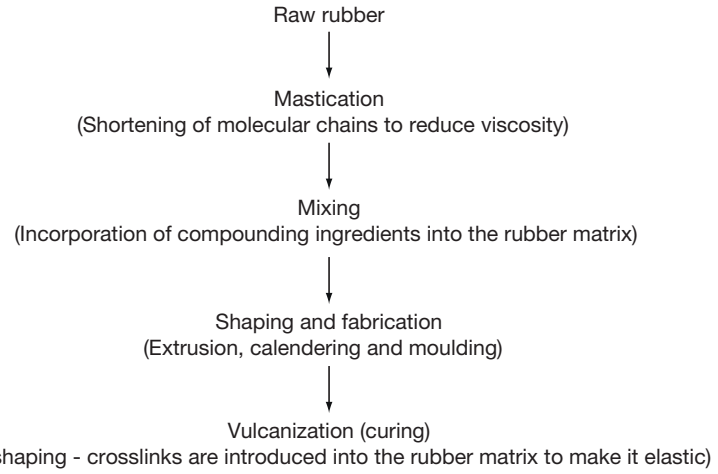
Raw rubber
Mastication
(Shortening of molecular chains to reduce viscosity)
Mixing
(Incorporation of compounding ingredients into the rubber matrix)
Shaping and fabrication
(Extrusion, calendering and moulding)
Vulcanization (curing)
(Final shaping - crosslinks are introduced into the rubber matrix to make it elastic)

Figure 5 Schematic flow process chart.

satisfy service performance; (ii) to be able to meet processing characteristics for efficient utilization of available equipment, and (iii) to meet conditions (i) and (ii) at the lowest possible cost. In other words, the most important criteria in compounding are to secure an acceptable balance among demands arising from the three concerned areas.

Theoretically, a rubber compound may consist of an elastomer and a cross linking agent. However, in practice, a rubber compound may contain 5 ingredients or even more than 10 ingredients, depending on the intended products, types of application and their service conditions. Each ingredient has a specific role and function(s). Each has an impact on properties, processability, and price. The real challenge is to develop a high quality rubber product at the lowest cost possible. The materials utilized by the rubber compounder can be classified into nine major categories, which are defined as follows:

- *Elastomers*: The basic component of all rubber compounds may be in the form of rubber alone, or master batches of rubber–oil, rubber–carbon black, or rubber–oil–carbon black.
- *Vulcanization agents*: These materials are necessary for vulcanization processes where chemical crosslinks are introduced into the rubber matrix to form a three-dimensional network. Crosslinks inhibit permanent flow under deformation or heat and prevent dissolution in solvents. Strength, stiffness and resilience increase upon cross linking, and set, stress-relaxation and creep decrease.
- *Accelerators*: In combination with vulcanizing agents, these materials reduce the vulcanization time (cure time) by increasing the rate of vulcanization. In most cases, the physical properties of the products are also improved.
- *Activators*: These ingredients form chemical complexes with accelerators, and thus aid in obtaining the maximum benefit from an acceleration system by increasing vulcanization rates and improving the final properties of the products.
- *Age-resistors*: Antioxidants, antiozonants, and other materials are used to slow down ageing processes in the vulcanizates.
- *Fillers*: These materials are used to reinforce or modify physical properties, impart certain processing properties, and reduce cost.
- *Processing additives*: Formerly known as processing aids, the new term currently used is processing additives. These are materials used to modify rubber during the mixing or processing steps, or to aid in a specific manner during extrusion, calendering, or molding operations.
- *Softeners*: They are materials that can be added to rubber either to aid mixing, produce tack, or extend a portion of the rubber hydrocarbon (e.g., oil extended).
- *Miscellaneous ingredients*: These materials can be used for specific purposes but are not normally required in the majority of rubber compounds. They include retarders, colors, blowing agents, abrasives, dusting agents, odorants, etc.

3.33.4.3 Vulcanization

Vulcanization is a process of cross-linking rubber molecules chemically with organic/inorganic substance through the action of heat and pressure. The

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rubber which is cross linked chemically is known as vulcanizate. The introduction of crosslinks into the rubber matrix may be comparatively few in number but are sufficient to prevent unrestricted flow of the whole molecules past neighboring ones. The low concentration of crosslinks implies that the vast majority of the segments making up the long chain molecules are free to move by virtue of kinetic energy. An unvulcanized rubber dissolves completely in its solvent. In contrast, a vulcanized rubber only swells. The chemical crosslinks prevent complete dissolution. A vulcanized rubber in this sense is a solid and will retain its shape and dimensions.

Vulcanization is a very important process in the rubber industry and conducted at relatively high temperatures (140–200 °C). For latex dipped goods, vulcanization is conducted at relatively low temperatures (60–120 °C) and requires no pressure as the latex is in fluid form and flows to take the final shape of the former and mold.

One of the most important chemicals in vulcanization is the cross linking agent. Elemental sulfur is the most widely used cross linking agent in the rubber industry because it is very cheap, abundant and easily available. Besides, sulfur is very easy to mix and readily soluble in the rubber. By varying the amount of sulfur to the accelerator ratio one can get different types of crosslink in the rubber matrix. **Table 7** summarizes the types of sulfur vulcanization system,[10] nature of crosslinks produced and their influence on technological properties. Thus sulfur vulcanization provides flexibility as one can control the type of crosslink intended for specific use or applications. The most basic requirement for sulfur vulcanization is the availability of double bonds on the rubber hydrocarbon. The nonsulfur cross-linking agents include organic peroxides, quinines and their oximes and imines, metallic oxides and high energy radiation. The detailed mechanisms of vulcanization with these vulcanizing agents are discussed by Elliot and Tidd.[10]

There is another type of sulfur vulcanization system known as soluble efficient vulcanization (EV)[10] intended for engineering products that require consistent stiffness, low creep, low stress-relaxation and low set. This vulcanization system employs certain soluble accelerators, activators, and sulfur that completely dissolve in rubber giving a truly homogeneous compound.[10] In practice, this is achieved by selecting accelerators and activators that have a fairly high solubility in rubber at room temperature. Suitable accelerators for soluble EV include diphenyl guanidine, tetrabutylthiuram disulphide and *N*-oxydiethylenebenzothiazole-2-sulphenamide. Zinc oxide is insoluble in rubber, but it has to be included in the system as it plays a major role in sulfur vulcanization. However, 2-ethyl hexanoic replaces the common coactivator stearic acid as the latter reacts with zinc to form an insoluble zinc stearate which induces creep and the former forms a rubber-soluble zinc salt. The sulfur dosage employed in soluble EV must not exceed 0.8 pphr (parts per hundred of rubber) to ensure that it remains dissolved in the rubber and with no tendency to bloom to the rubber surface.

Nonsulfur vulcanization such as the peroxide vulcanization system produces carbon–carbon type of crosslink that gives excellent heat aging resistance and very low compression set. However, the mechanical strengths are lower than polysulfidic and monosulfidic crosslinks. The choice of vulcanization system depends on the service environment as well as the mode of deformation for the intended rubber product.

3.33.5 Rubber-to-Metal Bonding – Engineering and Automotive Applications

Most of the rubber springs involve bonding of rubber to metal. In many cases the metal parts are required for fixing purposes, particularly those of automotive components such as rubber bushes, engine mounts

Table 7 Sulfur vulcanization systems, types of crosslink produced and their effect on technological properties

Vulcanization system	*Sulfur*	*Accelerator*	*Type of crosslink*	*Technological properties*
Conventional	2.0–3.5	1.0–0.4	Polysulfidic	Increase tensile and tear strengths, high compression set, and poor heat aging
Efficient (EV)	0.3–0.8	6.0–2.5	Monosulfidic	Excellent heat aging, low compression set, low tensile, and tear strengths
Semi-EV	1.0–1.7	2.5–1.0	Mixtures of poly, di- and mono	Compromise or balance in terms of strength and heat aging

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and couplings. **Figure 6** shows some typical rubber-to-metal bonded products. In tank lining, the main function of rubber is to protect the metal against attack by corrosive chemicals as well as to protect the metal parts from oxidation by air and moisture, which leads to rusting.

The laminated rubber bearing consists of alternate layers of metal plates. The metal plates serve to restrain the lateral expansion of the rubber on compression. Because of restriction at the rubber metal interface, due to friction or when the rubber is bonded to metal, the rubber bulges at the end plates to maintain a constant volume. As a result, the effective compression modulus is dependent on the shape factor, S, defined as the ratio of loaded area to force free area.[2]

$$S = \text{Loaded area}/\text{Force free area} \quad [3]$$

For a rectangular rubber block of length L, width W, and thickness h, shape factor S is given by eqn [4]:

$$S = LW/[2h(L + W)] \quad [4]$$

The dependence of the compression modulus on the shape factor has a significant advantage where the vertical stiffness increases substantially, by inserting horizontal metal spacer plates into the rubber. For a rectangular rubber block having length L, width W, and height h, the shear stiffness and compression stiffness are given by eqns [5] and [6] respectively.

$$k_s = GA/h \quad [5]$$

$$k_c = 3G(1 + 2S^2)A/h \quad [6]$$

Here, G is the shear modulus of the vulcanizate and A is the cross-sectional area of the rubber surface subjected to shear or compression. Equation [6] shows

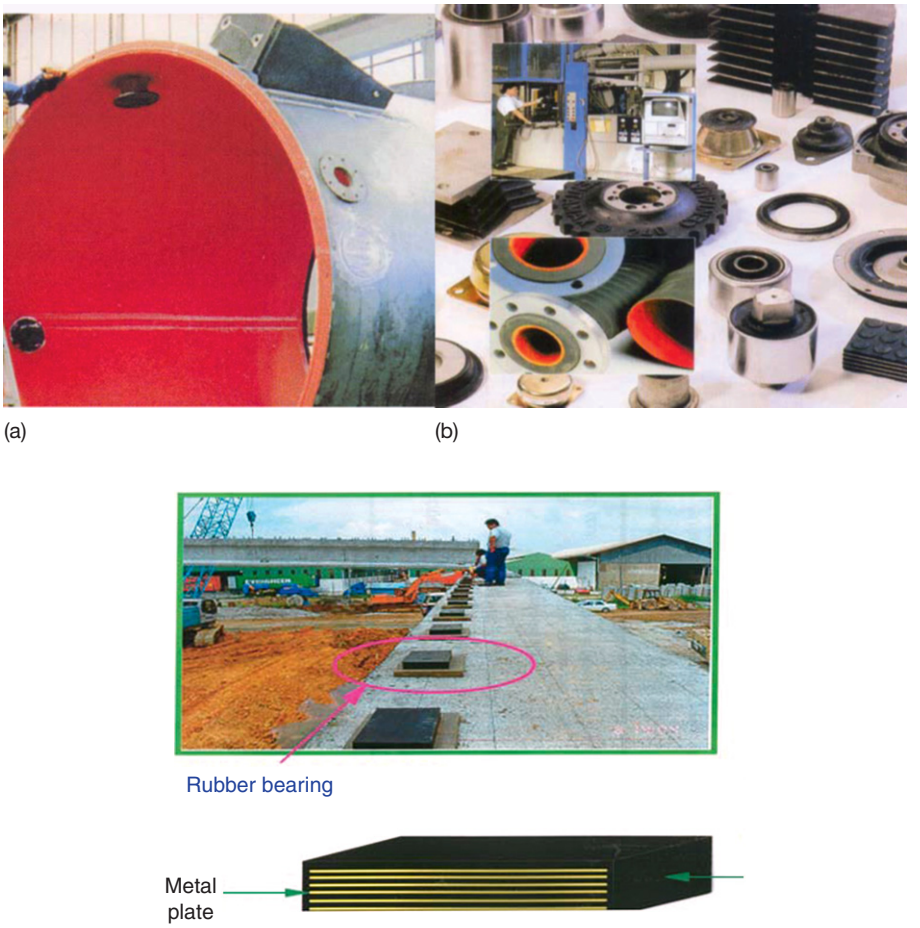

Figure 6 Rubber-to-metal bonding products – (a) tank lining (LHS), (b) various automotive rubber products (RHS) and (c) below rubber bridge bearing.

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that the compression stiffness can be increased substantially by increasing the shape factor. The shape factor does not affect shear stiffness. For these reasons, laminated steel rubber bearings are used in bridges, where high compression stiffness is necessary to support all dead and live loads of the deck, and very low shear stiffness to accommodate movements associated with thermal expansion and contraction due to temperature changes.

To achieve efficient bonding at the rubber–metal interface, it is necessary that the rubber is chemically bonded to the metal surface. This is achieved in practice by following proper procedures laid down in the following section.

3.33.5.1 Bonding of Rubber to Metal

3.33.5.1.1 Preparation of metal plates

The metal plates must be clean and free from any contamination such as oil, grease, protective coating, and rust. Exposing the contaminated metal surface to the vapor of a suitable organic solvent (e.g., chlorinated solvent) removes oil and grease. The next step is to remove metal oxides and rust on the metal surface, usually by the sandblasting technique or wire brushing. Apart from cleaning, sandblasting increases the surface area, which is very beneficial for strengthening the bonded area. Acid etching provides an alternative means of removing metal oxides from the metal surface.

It is very vital that the metal surface is completely free from oil, grease and rust to ensure efficient wetting of the bonding agent on the metal surface so that during vulcanization the bond formed between rubber and metal via the bonding agent is very strong. However, a few precautions need to be observed when sandblasting on the metal surface. The grit size, gun pressure and shooting distance must be correct to get the right surface topology, thus avoiding excessive wear or too little wear.

3.33.5.1.2 Types of bonding agent and methods of applications of bonding agent to metal plates

The common bonding agents for bonding rubbers to metals include ebonite solution or sheet, brass and proprietary adhesives. In the past, the bonding agent as well as the lining material for making tank lining was ebonite solution and calendered ebonite sheet. The ebonite compound contains a high amount of sulfur, about 25–35 pphr. This high sulfur content makes ebonite a hard and brittle material. Indeed ebonite is a thermoset as it is highly cross linked. The high sulfur content of ebonite introduces high polarity that makes it a very suitable bonding agent. Despite the superior chemical resistance of ebonite, there are a few limitations such as its brittleness after cure, long cure time and potential of fire hazard due to exothermic reaction during curing, especially when a thicker lining is involved. For this reason, soft rubber linings are preferred to ebonite linings.

Brass is a very good bonding agent, and is widely used in the tire industry. Brass is coated on steel wire cords by the electroplating process. Brass-coated steel wire cords are used as breakers or belts placed underneath the tread and on top of the carcass of the green tire. During vulcanization, the sulfur forms covalent bonds with both the rubber and the component metals of the brass, leading to a very strong bond.[11]

In most rubber-to-metal bonded products, a proprietary bonding agent is preferred to the other two bonding agents. A proprietary bonding agent usually requires two coatings, *viz.* a primer and an adhesive cement. There are reasons why a two-coat system offers more insurance for the rubber to metal bond. The first coating known as a primer helps to eliminate corrosion in corrosion-prone metals when they are in contact with the rubber.[12] By using a primer, secondary cement (second coating–adhesive) that has a greater degree of bondability to the stock being used can be selected, rather than a one-coat system.[12] It is claimed that the two-coat system allows more metal adhesion into the primer, and more stock adhesion into the cement coat.[12] This results in a higher intrinsic bond with the two-coat system than a single coat system.

Bonding agents are applied by painting, spraying or dipping on treated metal parts in the form of a solution or aqueous suspension.

3.33.5.1.3 Molding of rubber-to-metal bonded parts

Finally, the dried, coated metal parts are loaded into the mold and the rubber is vulcanized in contact with these substrates by the conventional rubber molding techniques such as compression, transfer and injection molding. It is during this vulcanization process that the rubber is chemically bonded to the metal surface when the cross linking agents react with the adhesive.

However, in the case of tank lining, the method is different from the conventional rubber-to-metal bonded products. The method of applying calendered rubber sheeting onto the prepared metal surfaces is

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analogous to that of applying rolls of wallpaper to the walls of a room. However, care must be taken to avoid entrapment of air between rubber and metal. The rubber sheet is laid down at the correct angle, and is rolled down into close contact with the adhesive. Applying the rubber sheet at the corner or edges of the tank is quite tricky. In practice, this is achieved by making joints at corners by inserting and rolling down an extruded rubber fillet of triangular cross-section and forming the sheet joints on top of the fillet. This technique gives to the lining a well finished appearance and reduces the danger of weak joints occurring in corners.

Upon completion of laying the rubber sheet onto the metal surface, the covered lining tank is usually allowed to rest for at least 24 h before being vulcanized. This resting period allows any air trapped between rubber and metal to diffuse, apart from enabling the adhered rubber sheet to recover and settle down before it is heated.

3.33.5.2 Vulcanization

It is usually done in an open steam autoclave for tanks or vessels that are small enough to go into the autoclave. When the lined vessel is too large to be accommodated in an autoclave it may be vulcanized in one of the following methods:

3.33.5.2.1 Low or high pressure steam

This method is applicable to a vessel that has sufficient strength to withstand internally applied pressure. This procedure can be adopted if the vessel such as road or rail tank cars can be lined and then sealed and bolted to give a strong and steam proof pressure container. The steam pressure is passed through the lined vessel to the desired vulcanization temperature until the rubber is fully vulcanized. There are some elements of danger when dealing with high pressure steam. So it is very important that all the safety regulations are met in terms of design and material of the vessel. The work should be done under skilled engineering supervision.

3.33.5.2.2 Water curing technique

This method is suitable for tanks or vessels that are too weak structurally to be put under steam pressure. Here, the lined tank is filled with water or brine. The water is heated by passing live steam into the water until it approaches boiling point. This temperature is maintained for a few hours until the rubber is fully vulcanized. Care must be taken to ensure that live steam does not impinge on the rubber lining to avoid the occurrence of a large blister between the rubber and metal at the point of impingement. It is necessary to conserve heat by shielding the unit against draughts and cold to minimize temperature variations which would affect the uniformity of the cure.

3.33.5.2.3 Hot air or ambient temperature vulcanization

This method is suitable for tanks or vessels which do not work with the methods discussed above. The choice of accelerator is very important. Ultrafast or very fast accelerator is usually used in the rubber compound. Care has to be taken to ensure that the rubber does not vulcanize prematurely (scorched) before it is applied onto the treated metal surface. One of the means to overcome the problem is to avoid mixing the accelerator and sulfur together, but to prepare sulfur masterbatch and accelerator masterbatch separately. The two masterbatches are blended together just prior to calendering, and the calendered sheet applied as soon as possible to the metal to avoid the risk of being scorched.

3.33.5.3 Types of Bond Failure and Possible Remedies

A rubber shear mount may be expected to deform up to 300% shear strain, and the mean shear stress acting on the rubber-to-metal bond can be as high as 10 MPa or 2/3 tons per square inch.[11] Steel laminated rubber bearings for bridges must have a minimum bond strength of about 9 N mm^{-1} (MS 671, 1991).

It is important to observe the failure mode that occurs in rubber-to-metal bonded products because it throws some light and clues to the root cause of the problem. It is usual to conduct peel test to determine the interfacial bond strength between the rubber and metal. There are two basic types of bond failure either adhesive or cohesive. Adhesive failure may occur at the interfacial between the rubber and substrate, or between cement and substrate. Cohesive failure occurs within the rubber itself. There are three modes of adhesive failure.[13] First is called CM failure that takes place between primer and metal interface. Second is CP failure that occurs at the primer to cover cement interfacial. Third is RC failure where the bond fails at the rubber–cover cement interface. RC failures are the most common and the most difficult to solve.[13] There are a number of causes, which bring about these bond failures. They include the following: metal surface not cleaned efficiently due to poor cleaning procedure,

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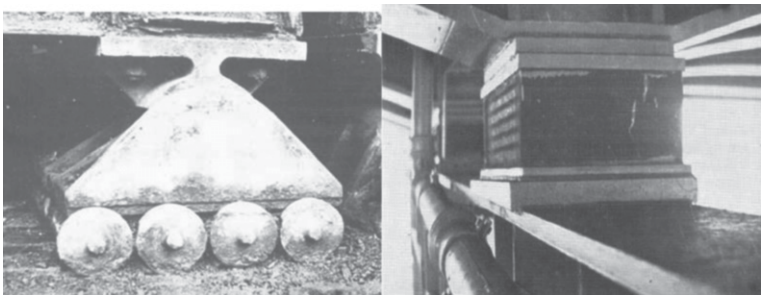
contamination of metal surface during handling, incomplete wetting of adhesive on the metal surface, variations of temperature of metal surface, precured adhesive, sweeping of adhesive during molding etc.[13] There are remedies to overcome these problems. First, ensure that the metal surface is free from all forms of contamination. Second, avoid contamination of metal surface during handling. Third, apply the primer and adhesive cement onto the metal surface evenly by taking care of the correct viscosity of the adhesive, and correct spraying distance and thickness of the adhesive film. Fourth, use the correct type of adhesive and follow strictly the instruction and procedure recommended by the chemical supplier.

If during the peel test, cohesive failure occurs within the bulk of the rubber, then this indicates that the interfacial bond strength between the rubber and metal plate via the bonding agent is stronger than the cohesive strength of the rubber itself.

3.33.6 Oxidation of Rubber

Metals oxidize in the presence of air and water and consequently they corrode, become rusty and weak. **Figure 7** shows the old version of using steel rollers to accommodate movements of the bridge deck brought about by expansion and contraction due to temperature changes.[14] The steel rollers corroded and suffered high wear and tear. In contrast, laminated steel rubber bearing did not show any sign of wear out after nearly twenty years of installation.[14] However, this does not mean that elastomeric bearing will last forever. Like metals, rubbers are also prone to corrosion. Corrosion of rubbers is associated with the aging process known as degradation. All unsaturated rubbers are subject to degradation due to the attack of heat, ultraviolet (UV) light, oxygen, ozone etc. The more is the amount of unsaturation the more it is susceptible to degradation. The term aging as applied to rubber, covers a variety of phenomenon arising out of the factors described above. Aging properties of raw rubber differ from vulcanized rubber because of the latter's specific network structure and extra network material. When natural rubber is heat-aged in the presence of oxygen or air, it invariably loses strength, in particular its tensile strength decreases. The pattern of modulus change during aging is not so straight forward because there are two opposing reactions which can occur simultaneously. One is degradation of the molecular chains and crosslinks which causes softening; the other is additional cross linking which causes stiffening. Under any given set of aging conditions (time and temperature) either softening or stiffening reactions may predominate depending on the type of vulcanization system, type of filler and antidegradants employed in the rubber compound.

Oxygen reacts with rubber only after the rubber has been acted upon by energy. This is usually from UV light, heat or mechanical energy (flexing). This energy dislodges a hydrogen atom from the rubber molecule, resulting in the formation of a radical. The oxidation of polymer with elemental oxygen is called autoxidation because it is an autocatalytic. The rate of autoxidation is affected by temperature, the presence of catalyst and also the presence of antioxidant. When the oxygen attacks the rubber it produces hydroperoxide. The hydroperoxides break to form free radicals. This is an autocatalytic, self generated free radical process. The autoxidation process involves three main stages, namely, initiation, propagation and termination. In view of the complexity of autoxidation reaction with rubber, Bolland and Gee[15,16] used model olefins to study the kinetics of autoxidation. **Figure 8** shows the mechanism of autoxidation as proposed by Bolland.[15,16]



(a) (b)

Figure 7 (a) Steel roller bridge bearing and (b) steel laminated rubber bearing installed in 1955. Adapted from Mullins, L. *Proc. Rubb. in Eng. Conf*. Kuala Lumpur, 1974, pp. 1–20, with permission from the Malaysian Rubber Board.

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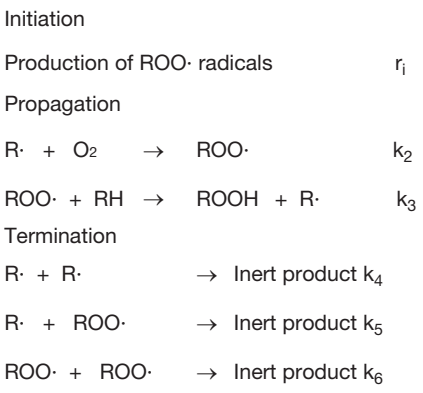

Figure 8 Mechanism of autoxidation of natural rubber as outlined by Bolland. Adapted from Barnard, D.; Lewis, P. M. In *Natural Rubber Science and Technology*; Robert, A. D., Ed. Oxford University Press, 1988; Chapter 13, pp 621–673, with permission from · · ·.

The autoxidation is initiated with the generation of free radicals due to the relatively facile homolysis of traces of peroxide present in the elastomer.[17] The rate of oxidation is related to the concentration of the hydroperoxide [ROOH] as shown by eqn [I] below[16].

$$r_i = k_i[\mathrm{ROOH}]^2 \qquad [\mathrm{I}]$$

The resultant free radicals react with oxygen to form the deleterious peroxides and propagate the autoxidation reaction. The rate of propagation is controlled by the hydroperoxide yields and those of decomposing. The hydroperoxide yields for a large number of olefins range from almost 100% downwards to values controlled by side reactions of the peroxy radicals, such as addition to olefinic double bonds, when hydrogen abstraction becomes relatively difficult.[16] Such side reactions would continue the propagation chain. However, when the value of the rate constant k_2 becomes large, the reaction of alkenyl radicals with oxygen become independent of oxygen pressure. Under these conditions, rate-determining step is no longer controlled by the rate constant k_3, of the hydrogen abstraction step. Termination would occur primarily by the interaction of alkenyl radicals. Then the propagation rate is given by eqn [II] below[16].

$$r = r_i^{1/2} k_2 k_4^{-1/2}[\mathrm{O_2}] \qquad [\mathrm{II}]$$

Termination occurs solely by the mutual destruction of peroxy radicals and represented by the following rate equation[16]:

$$r = r_i^{1/2} k_3 k_6^{-1/2}[\mathrm{RH}] \qquad [\mathrm{III}]$$

The outcome of this autoxidation is either chain-scission or cross-linking. If chain-scission occurs, the degraded rubber will be soft and tacky. On the other hand, if cross linking occurs the degraded rubber will be hard and brittle. In both cases, the mechanical strength of the rubber decreases markedly. Model olefins were used to study the mechanism of oxidation of NR due to complexity of the oxidation reaction in particular when the rubber is vulcanized.[16] The oxidation of rubber vulcanizate is technologically important since the absorption of only a small amount of oxygen (1%) by rubber vulcanizate results in a considerable change in the physical properties.

It is believed that the oxidation of natural rubber follows the same route and analogous to that of the model olefins where the polyisoprene chain undergoes scission.[16] An essential concept of this process is the number of molecules of oxygen absorbed per scission event. According to Bolland,[15] the oxidation reaction would finally lead to an alkoxy radical disproportionate to butan-2-one-4-al rather levulinaldehyde, and the vinylic radical would have to be oxidized further to the methyl ketone end group. Minute amount of certain heavy metals such as copper, iron and manganese catalyze autoxidation reactions. However, this catalytic action can be prevented by applying protective or chelating agent such as metal deactivator like *p*-phenylenediamines.

In the case of vulcanized rubber, the oxidation reaction is more complex than that of raw rubber since the various different types of crosslink (e.g., ploysulfidic, disulfidic, monosulfidic, cyclic sulfides, conjugated dienes and treines, etc.) present in the network structure may affect oxidation in some way or another.[16] Most types of sulfur vulcanizates initially hardens on aging before degradation occurs. This hardening is due to cross linking associated with oxidative reactions of sulfur species in the network that takes place before chain scissions take place.[16]

Barnard and Lewis[16] listed out some useful and important points concerning chain scission mechanism for unprotected NR at modest temperature as follows:

- Scission occurs once approximately for every 20 molecules of oxygen absorbed.
- The scission is of the rubber chain even in peroxide or sulfur vulcanizates although concomitant crosslink can occur in the latter.
- Kinetically, scission appears to take place in the propagation step.

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- Each scission event results in a stable terminal ketone group being formed on one of the new chains and a transient terminal aldehyde group on the other.

Since autoxidation results in chain scission, means and ways were introduced to determine accurately chain scissions caused by a known quantity of oxygen absorbed. A parameter known as scission efficiency ε defined as the number of molecules of oxygen absorbed which bring about one scission event[16] was introduced to monitor chain scission quantitatively. There are two methods either physical or chemical to monitor chain scission. The common physical methods involved measuring molecular weight reduction, stress-relaxation, sol–gel analysis, and stress–strain characteristics.[16] For example, in stress-relaxation method, a rubber sample of a uniform cross-section is held at a constant extension and maintained at a constant temperature. When a network is oxidized due to the cleavage of stress-supporting chains, then the stress would decay and this event would lead to occurrence of stress-relaxation. The change in moles of stress-supporting chains per gram can be calculated from eqn [7][16]:

$$f_t/f_0 = N_t/N_0 \qquad [7]$$

where the subscripts t and 0 refer to the samples after time t and time zero respectively, and f derived from the statistical theory of rubber elasticity[18] is given by eqn [8]:

$$f = \rho NRTA_0(\lambda - \lambda^{-2}) \qquad [8]$$

where ρ is the density of rubber, N is the number of moles of stress-supporting chains per gram, R is the gas constant, T is the absolute temperature, A_o is the unstrained cross-sectional area, and λ is the extension ratio. Stress-relaxation method has the advantage of being able to monitor scission event continuously, and if the amount of oxygen absorbed is also known then the scission efficiency ε can be calculated.[16] However, on a short time scale, the decay in stress level as function of time at constant deformation and temperature is associated with the rearrangement of molecular chains and it is predominantly attributed to viscoelastic behavior of the rubber.

Almost all technical specifications of elastomeric products require passing an aging test. The use of aging tests is extremely important in assessing the service life of elastomeric products because properties of vulcanizate could change during service. The basic principle of the test is to expose rubber test-pieces to air at an elevated temperature (70 or 100 °C) for a specified period (7 or 14 days or longer). This so-called accelerated aging test causes deterioration of rubber in air due to combined effects of oxidative and thermal aging. The tensile properties, set and hardness are measured on these samples before and after ageing. If minor changes in these properties result, long service life may be expected; if appreciable changes occur, service life may be short. However, it must be stressed here that accelerated ageing test is a useful quality control and specification tests. There are significant difficulties in predicting service life from accelerated aging test. Use of test temperatures much above the anticipated service temperature is not advisable because the correlation between the results of such tests and service performance becomes increasingly tenuous.

3.33.7 Ozone Cracking of Rubber

Apart from oxygen, all unsaturated elastomers are also susceptible to ozone attack although ozone concentration in the outdoor atmosphere at ground level is about 1 pphm (part per hundred million of air by volume).[19,20,21] However, this can be significant because the reaction of ozone with the double bond is extremely fast and causes cracking on strained rubber. The cracks appear slowly at right angle to the direction of the strain applied, that grow slowly and consequently lead to a break of the vulcanizate. Ozone being very reactive attacks the double bonds of the rubber and produces ozonide that cleaves to produce zwitterions.[17] The zwitterions are unstable and will breakdown to form other zwitterions. These zwitterions may react with other zwitterions to produce diperoxide compound, or react with carbonyl compound to produce ozonide. In both cases, the ultimate result is chain scission. The mechanism of ozone attack on olefin is as shown in **Figure 9**.[17]

However, there is a subtle difference between ozone cracking and auto-oxidation where the former requires a certain critical strain level (~5% for unprotected NR) for its occurrence.[19,20,21] The severity of ozone cracking increases rapidly with strain level. Braden and Gent,[19] and subsequently Lake *et al.*[20,21] investigated various factors affecting ozone cracking. For example, Lake and Thomas[20] came out with a boundary layer theory for ozone attack on rubber surface to explain the rate of ozone crack growth. According to their theory, the variation in

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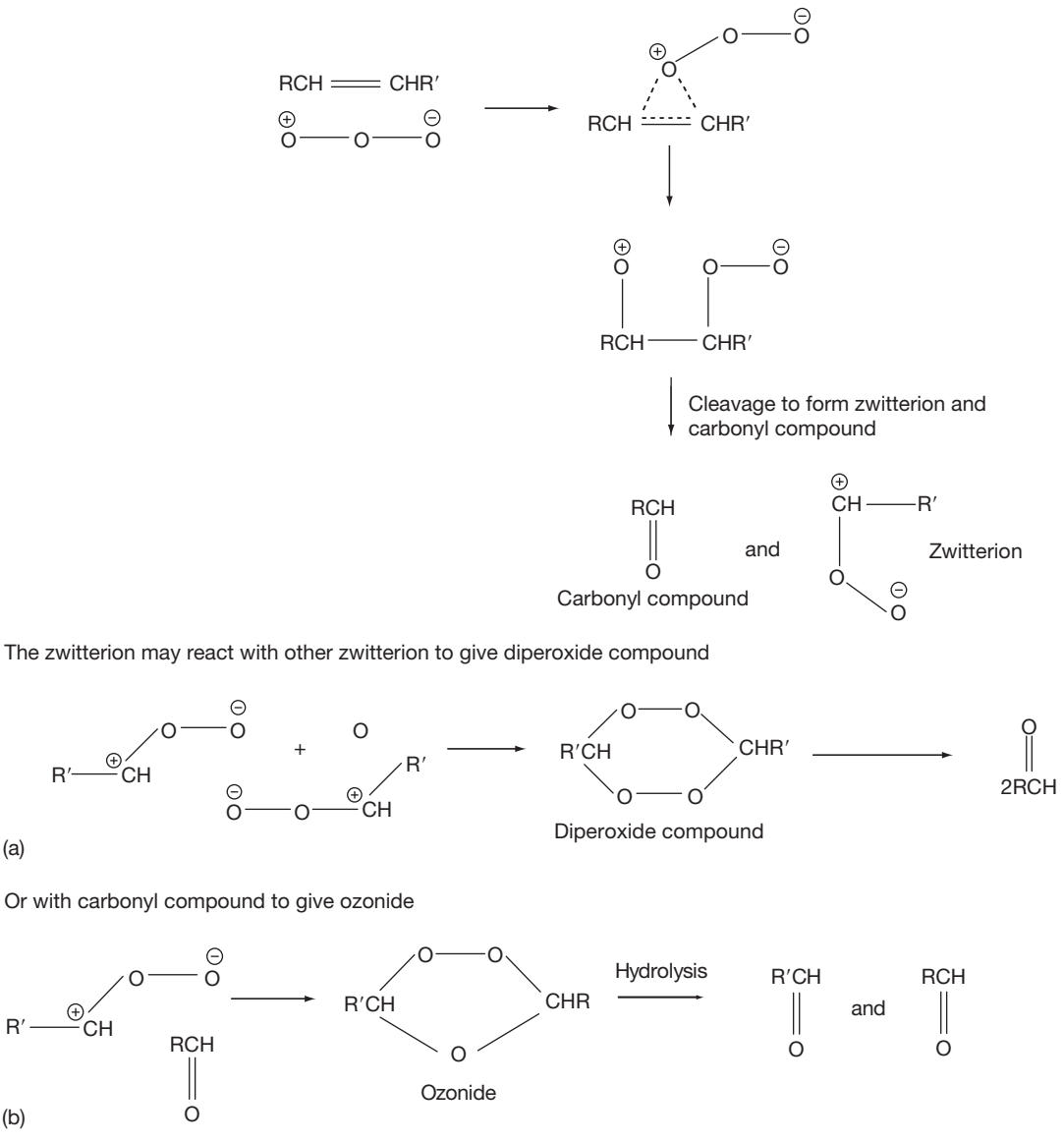

Figure 9 Mechanism of ozone attack on olefins.

the rate of ozone attack on stretched rubber surfaces produced by changes in the air velocity and magnitude of the strain is controlled by the diffusion of ozone across the relatively stationary boundary layer adjacent to rubber surface. The boundary layer effect is important because of the readiness with which ozone is destroyed by stretched rubber.[20] As mentioned earlier, ozone cracking occurs only in elastomers subject to tensile stresses. Elastomeric components used in compression will crack only in the regions of the surface where tensile stresses are induced. These cracks are unable to penetrate very far because they soon encounter compressive rather than tensile stresses. Thus ozone cracking is not a serious problem for large elastomeric components such as rubber bearings which are used in compression. Nevertheless, ozone cracks are unsightly and may initiate fatigue crack growth, which ultimately leads to mechanical failure. In view of this deleterious effect, it is necessary to carry out test on ozone resistance. The test involves exposing the stretched test-pieces (20% strain) in an ozone-rich atmosphere at a fixed temperature (23 or 40 °C) and inspecting the surfaces for cracks with the aid of a magnifying

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glass at intervals of time. If cracks are not observed after completion of test, the vulcanizate is said to have good resistance to ozone cracking.

3.33.8 Heat Aging Resistance

Elastomers can survive over long periods in service at ambient temperatures without any measurable deterioration if the products are sufficiently thick. For a thick section of rubber, the availability of oxygen will be limited by diffusion, and components with bulky rubber layers can be considerably more resistant to elevated temperatures than thin rubber sections. For example, bearing pads of NR installed in 1890 had been examined, and although the outer 1–2 mm of rubber had degraded after 96 years of exposure to the atmosphere, the inner core of the rubber was still in good condition as shown by the photograph in Figure 10.[2] Rubber samples taken from the interior portion were found to retain good physical properties as that of freshly prepared compounds.[2] At sufficiently elevated temperatures, all types of elastomer will undergo degradation. However, conventional NR vulcanizates can be used safely at 60 °C, the maximum ambient temperature likely to be encountered practice.[2] At temperatures of 300 °C and above, NR vulcanizates first softens as molecular breakdown occurs, then resinify, becoming hard and brittle.[2] Flammable vapor are emitted and ignition occurs. However, the rate of burning is extremely slowly for the case of large block rubber.[2]

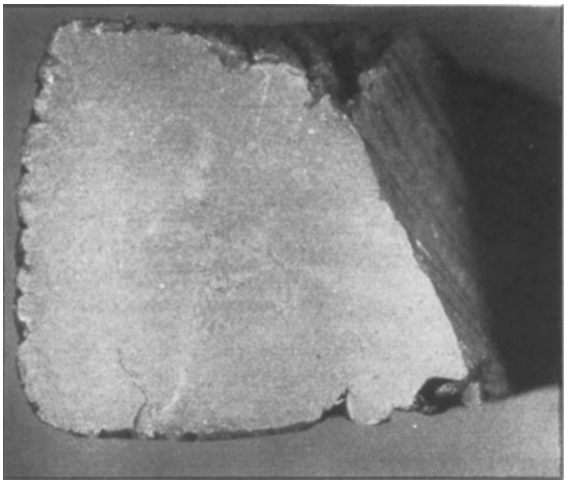

Figure 10 Cross-sectioned view of a 100-year old bridge bearing pad showing the very small depth of penetration of atmospheric degradation. Adapted from Fuller, K. N. G.; Muhr, A. H. *Engineering design with natural rubber, NR Technical Bulletin*, 5th ed.; The Malaysian Rubber Producers' Research Association, London, 1992; pp 1–33, with permission from Tun Abdul Razak Research Centre, Brickendonbury Hertford, England.

In recent years, new performance demands for automotive elastomers have been proposed[22] to perform at high operating temperatures. This move was made to accommodate increasing concern for improved fuel economy, which resulted in a significant downsizing and redesign of the automobile. Concomitantly the engine compartment became smaller and more difficult to cool thus raising the temperature of the under hood. Current automotive elastomers are expected to perform well under a 120 °C in-service temperature at least until the life of the car.[22]

There is a growing expectation those future automotive elastomers to perform well in a 150 °C environment for over 100 000 miles.[22] This is a clear signal that specialty elastomers would find very strong markets over general-purpose elastomers for high temperature performance.

3.33.9 Flex Cracking

Flexing and cyclic stresses can lead to premature failure during service. There are two basic mechanisms of crack growth, (i) ozone crack growth, due to primarily chain scission, and (ii) mechanico-oxidative crack growth, due to mechanical rupture at the tip of a flaw, which is considerably facilitated by the presence of oxygen.[23] Both types of growth can occur under static or dynamic conditions or together. The amount of crack growth in a given time is directly proportional to the ozone concentration. The crack growth rate dc/dt of a single ozone crack under static conditions is given by eqn [9]:

$$dc/dt = \alpha q \qquad [9]$$

where q is the ozone concentration and α a constant (the rate at unit ozone concentration) which is a property of the rubber.[23] The cyclic crack growth rate is given by eqn [10]:

$$r = (dc/dn)\text{ozone} = (F/f_f)\alpha q \qquad [10]$$

where F is the time fraction of cycle for which the test-piece is strained, and f_f is the frequency.[23] Based on fracture mechanics approach, and assuming that the growth of naturally occurring flaws of a fatigue test has the same characteristics as that of a crack growth test, Lake and Lindley[23] worked out

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the fatigue life of vulcanized elastomer as given by eqn [11]:

$$N_f = 1/(16BW_s^2c_0) \qquad [11]$$

where N_f is the number of cycles to failure from a naturally occurring flaw of size c_0. B is the crack growth constant, and W_s is the strain energy density. Thus the fatigue life N can be predicted from known parameters of eqn [11].

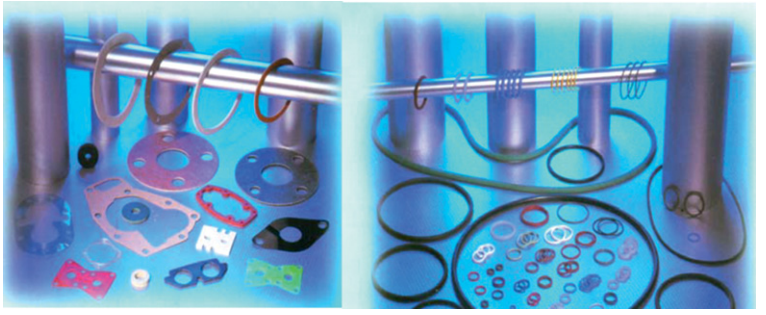
3.33.10 Oil Absorption

An unvulcanized elastomer becomes solution when immersed in its solvent; in contrast, a vulcanized elastomer will only swell. The extent of swell depends on the amount of solvent absorbed, which in turn depends on the crosslink concentration and types of solvent. Swelling is undesirable because apart from dimensional instability, the modulus and mechanical strengths are all decreased making the swollen vulcanizate unsuitable for most engineering applications.[2] In the case of rubber-to-metal bonded, bond failure occurs if the liquid is able to reach the metal plate. Figures 11 and 12 show some of the typical automotive elastomeric components such as fuel and oil hoses, gaskets, O-rings and seals which are in contact with automotive fuels. These rubber components are thin and susceptible to damages when swollen excessively by the oil. Additives such as ethanol, methanol, and methyl *t*-butyl ether are being placed in gasoline with a view to improve its octane number.[22] Increasing the alcohol content of the gasoline increases the amount of swell, which is very undesirable not only because of dimensional instability, but also reduces tensile strength and elongation at break of the swollen elastomer.

It is well established that swelling is diffusion-controlled and the volume of liquid absorbed is initially proportional to the square root of the time of immersion.[2] For most organic liquids, the rate of penetration depends on their viscosity rather than

(a) (b)

Figure 11 Automotive rubber products in contact with oil and heat: (a) hoses – hydraulic, fuel, gasoline pump, and steam hose and (b) gaskets, O-rings, seals, and exhaust hanger, etc.



(a) (b)

Figure 12 Automotive rubber components: (a) gaskets and (b) O-rings and seals.

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their chemical nature[2]. **Figure 13** shows the time–viscosity relationship for the liquid to penetrate 5 mm into the rubber interior.[2]

For NR, it takes about 4 days for a volatile liquid such as toluene to penetrate 5 mm depth, 1–2 years for engine lubricating oil, and about 30 years for a petroleum jelly, even with continuous immersion.[2] It is possible to estimate the distance of liquid in a given time provide that the penetration rate is known.[2] Alternatively, the viscosity of the liquid may be used if penetration rate is not known since the penetration rate is related to viscosity as shown earlier in **Figure 13**.

Southern[24] has introduced a nomogram as illustrated in **Figure 14** to facilitate the calculation in estimating the penetration depth of liquid into the elastomer. Although the data were obtained for NR, but would be expected to work with other elastomers of similar T_g.[24] As an illustration to use the nomogram, Southern[24] has calculated, a liquid with penetration rate of 7×10^{-5} cm $s^{-1/2}$ would take 4 weeks to penetrate 1 mm, but 100 years to penetrate 40 mm of the rubber block. The penetration rate–viscosity relationship does not hold for water because of the presence of hydrophilic impurities which complicate transport of water in elastomers.[24]

3.33.10.1 Effect of Crosslink Concentration and Polarity on Swelling Resistance

Natural rubber (NR) latex has found very wide applications in the glove industry since the 1920s. This is attributed to the excellent tear and puncture resistance of NR latex films. Besides, NR latex film exhibits very high extensibility (600–1000%) before its breaking point. These properties make NR latex film an excellent barrier protection against infectious liquids and gases. Most of the examination and surgical NR latex gloves are used in hospitals and clinics. However, recently NR latex gloves have entered the fast food industry where good swelling resistance is an essential requirement. Being a nonpolar rubber, NR latex gloves have a poor swelling resistance which limits its application in the fast-food industry. The fast-food industry is growing very fast all over the world. There is a growing concern over the cleanliness and hygiene of the food. It is essential that the workers wear rubber gloves to avoid contact with the food they serve. Rahim and Samsuri[25] investigated the effect of crosslink concentration and effect of blending carboxylated nitrile rubber (XNBR) with NR latex on the swelling resistance of NR latex film towards cooking oil. The amount of sulfur was varied to produce different crosslink concentrations. The crosslink concentration was determined by immersing the latex film sample in a solvent until equilibrium swelling was attained. The crosslink concentration was calculated by using the Flory–Rehner equilibrium swelling equation as proposed by Mullins[18] given by eqn [12]:

$$-\ln(1-v_r) - v_r - \chi v_r^2 = 2\rho V_1 [X]_{phy} v_r^{1/3} \qquad [12]$$

where v_r is the volume fraction of rubber in the swollen gel, ρ is the density of rubber, V_0 is the molar volume of solvent, χ the rubber–solvent interaction parameter, and $[X]_{phys}$ is the physically manifested crosslink concentration. The diffusion coefficient D was calculated from eqn [13][24]:

$$M_t/M_\infty = (2/l)(Dt/\pi)^{1/2} \qquad [13]$$

where M_t is the total amount of liquid absorbed per unit area of the sheet after immersion for time t, M_∞ is the amount of liquid absorbed after infinite time (in this case time to reach equilibrium swelling), and l is the half thickness of the film sheet. It is necessary to plot M_t against square root time as shown in **Figure 15** to calculate D in eqn [13].

The effect of crosslink concentration on the diffusion coefficient of cooking oil in the latex film is shown in **Table 8**.[25] The results show that increasing the crosslink concentration decreases the diffusion coefficient significantly. Increasing the sulfur content from 0.6 to 3 pphr increases the crosslink concentration by about 90%, which merely decreases the

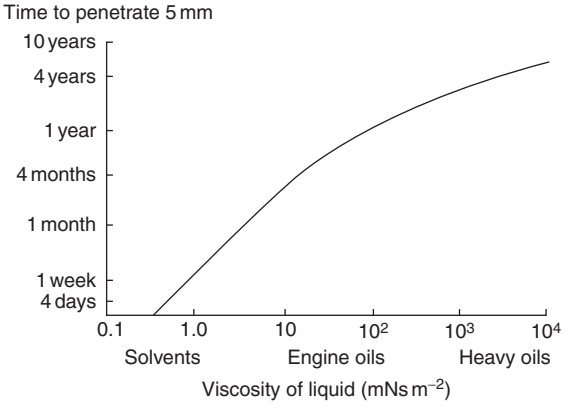

Figure 13 Effect of viscosity of liquid on penetration time. Adapted from Fuller, K. N. G.; Muhr, A. H. *Engineering design with natural rubber, NR Technical Bulletin*, 5th ed.; The Malaysian Rubber Producers' Research Association, London, 1992; pp 1–33, with permission from Tun Abdul Razak Research Centre, Brickendonbury Hertford, England.

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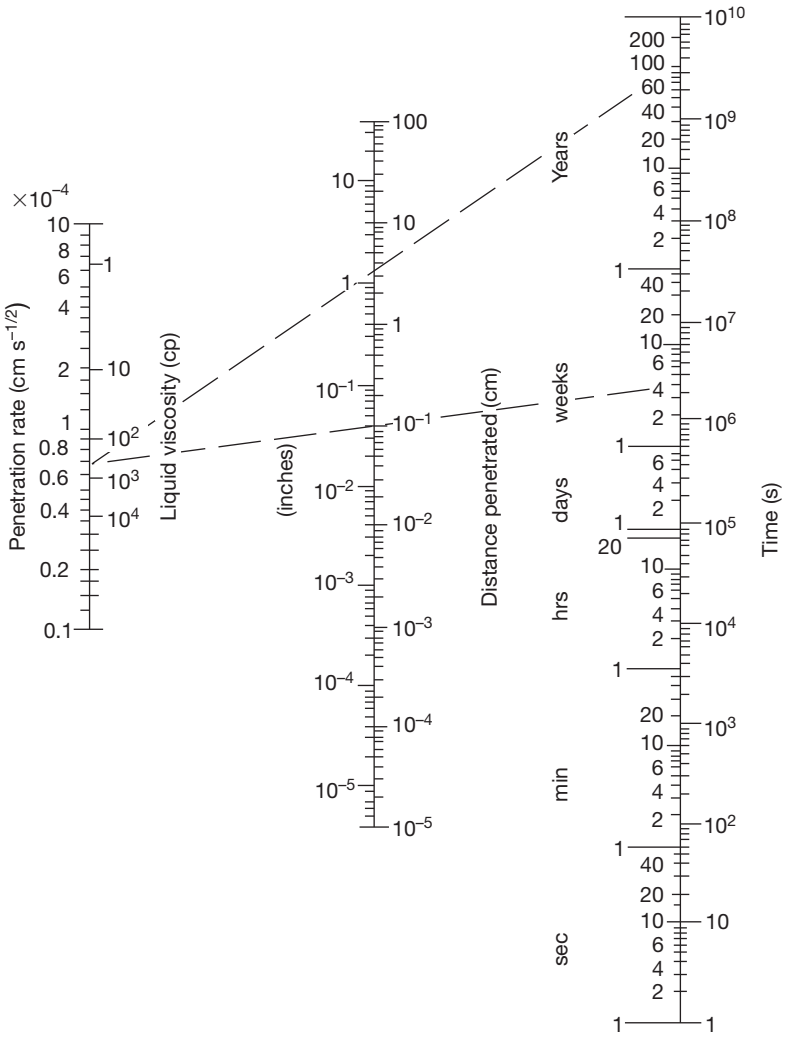

Figure 14 Nomogram to facilitate rapid calculation of distance penetrated by liquid into rubber. Adapted from Muniandy, K.; Southern, E.; Thomas, A. G. In *Natural Rubber Science and Technology*; Robert, A. D., Ed.; Oxford University Press, Oxford, UK, 1988; Chapter 13, pp 820–851, with permission from Oxford University Press.

diffusion coefficient by about 23%. However, the most efficient method to increase swelling resistance is through physical blending of NR latex with XNBR latex, where the diffusion coefficient D of the oil into the film decreases by a factor of 2.7 compared with NR latex having the highest crosslink concentration. Thus, this work shows strong evidence that blending of nonpolar elastomer with polar elastomer enhances the swelling resistance of the former.

3.33.11 Water Absorption

Elastomers find wide uses in marine and offshore engineering applications. The application of elastomers in water management is attributed to its high impermeability to water. A rubber sheet is used to line the water reservoir and pond, while inflatable rubber is used as a dam. Rubber dock fenders rely on the energy absorption capacity of the rubber. Inevitably, the rubber will absorb some quantity of water as these rubber products spend a considerable time under water. It is of great concern whether the absorption of water would impair the strength of the rubber.

The true solubility of water in rubber is very low.[24] Nonetheless, relatively large amounts of water can be absorbed during prolonged immersion as shown in **Figure 16**.[2] The diffusion of water in elastomers is not straightforward, but complicated by the presence of hydrophilic materials. In the case of NR it is mainly

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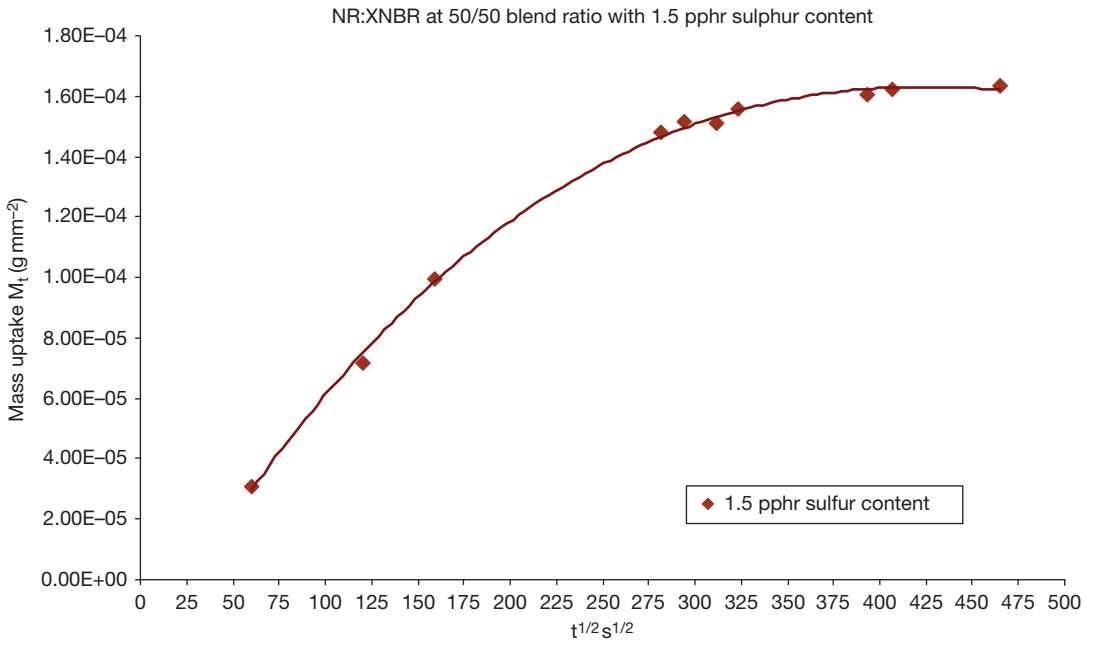

Figure 15 Typical mass uptake curve for NR/XNBR blend latex film.[25]

Table 8 Effect of crosslink concentration on diffusion coefficient *D* of cooking oil into NR latex film

Sulfur level (pphr)	*$[X]_{phy}$ (mol per kg RH)*	*D ($m^2s^{-1} \times 10^{-13}$)*
0.6	4.46×10^{-2}	4.70
1.0	4.60×10^{-2}	4.00
2.0	4.89×10^{-2}	3.70
3.0	5.82×10^{-2}	3.57
NR:XNBR (50:50) 1.5	–	1.30

proteinaceous.[24] When water diffuses into the rubber, the water-soluble hydrophilic materials dissolve forming droplets of solution within the rubber. Osmotic pressure gradient would exist between watery domains in the rubber and that of the external solution immersing the rubber.[24] This results in more water diffusing into the internal solution droplet. Water absorption reaches its equilibrium when the elastic stresses acting on the droplets balance the osmotic pressure difference. Muniandy and Thomas[24] proposed a mathematical model for water absorption to derive equations for the equilibrium water uptake and to evaluate the kinetics of water absorption and desorption. From the model, they calculated the equilibrium water uptake and the apparent diffusion coefficient. They found very good agreement between theory and experimental results.

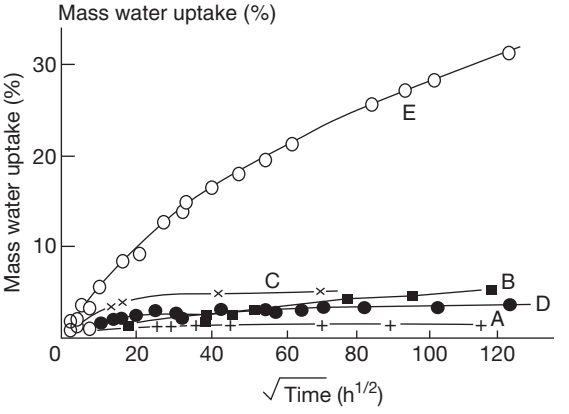

Figure 16 Corrected mass uptake measurements for engineering rubbers in seawater at 23 °C: (a) deproteinized NR, (b) lead oxide cured polychloprene, (c) nitrile rubber, (d) conventional NR, and (e) conventional polychloroprene Adapted from Fuller, K. N. G.; Muhr, A. H. *Engineering design with natural rubber, NR Technical Bulletin*, 5th ed.; The Malaysian Rubber Producers' Research Association, London, 1992; pp 1–33, with permission from Tun Abdul Razak Research Centre, Brickendonbury Hertford, England.

Later, Lake[26] investigated the kinetics of water (tap water) absorption in elastomers and their effects on properties. He reported that when the absorption was large (50% or more), the rubber test-piece degraded. Severe degradation leads to porosity of the surface layer, and when pressed, water exudes.[26] However, at a low level of absorption, Lake observed

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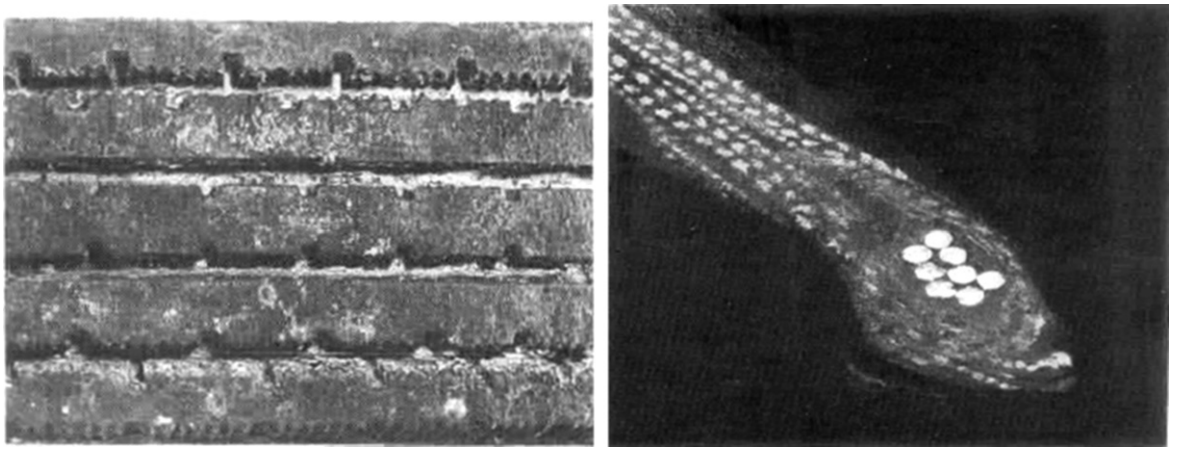

Figure 17 A natural rubber tire after 40 years' exposure to seawater. Adapted from Mullins, L. *Proc. Int. Rubb. Conf*. Kuala Lumpur, 1985, with permission from Malaysian Rubber Board.

the formation of droplets similar to the blisters that occur in plastics or under protective coatings, consistent with an osmotic diffusion mechanism.[24] In saltwater, water absorption reached steady state at much lower levels than in freshwater, again consistent with an osmotic pressure mechanism. Thus seawater is less damaging than freshwater and may not have any serious consequences for many elastomers. This latter point is consistent with findings of Ab. Malek and Stevenson[27] who evaluated the physical properties of a rubber tire as shown in **Figure 17**, recovered from seawater at a depth of 80 ft. They found that the rubber tire had absorbed about 5% of seawater after 42 years of immersion. They found no evidence of microbiological attack. What is more interesting, the physical properties of the rubber tire were within normal specifications for new rubber of the same type. They even suggested storing elastomers in deep seawater in view of its inert nature. Indeed, elastomer is a very suitable material to coat metal surfaces against corrosion in deep seawater. The photograph in **Figure 17** shows clear evidence that the steel cords making up the bead of the tire are corrosion-free after a 42-year immersion in seawater.[27]

3.33.12 Protective Measures

3.33.12.1 Selection of Elastomer

All elastomers experience aging. Some age faster than others. The rate of aging depends on a number of factors such as the chemical structure of the polymer, service environment, which includes length of exposure to heat and light, oxygen and ozone concentration, size and shape of elastomers, and mechanical stresses. One cannot stop the aging process, but one can slow it down. The most effective means of combating aging is to select the correct elastomers to meet the maximum service temperature and environment. Fully saturated elastomers having high bond dissociation energy making up their backbone chains are the best choice to meet high service temperature applications. Fully saturated rubbers such as ethylene propylene copolymer and very low unsaturation butyl rubber are excellent resistance to heat aging, oxidation and ozone cracking. Not only the maximum service temperature, but also other environmental factor such as oil or solvent determines the aging resistance. In cases like these, the elastomers having high bond dissociation energy and solvent resistance are desired. These include specialty elastomers such as acrylic (ACM), chloro-sulfonyl-polyethylene (CSM), ethylene propylene copolymer (EPM), fluoroelastomers (FKM), silicones (MQ, VMQ), polyester urethanes (AU), etc. Alternatively, for unsaturated elastomers are to use antioxidants and antiozonants, with correct vulcanization system can slow down the aging process quite efficiently.

3.33.12.2 Blends of Elastomers

It is a common practice to blend two elastomers of different properties with a view to combining the best features in terms of technical and economic values. Natural rubber is blended with EPM for applications requiring very high resistance to attack by ozone as the latter is fully saturated. A blend of NR and EPDM is used for applications that require a combination of good resistance to attack by ozone and high

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strength properties. Nitrile rubber (NBR) is blended with EPM to meet the requirements for very good oil resistance as well as conferring high resistance to oxidation and ozone cracking. The former is polar rubber and provides very good oil resistance, while the latter provides excellent weather resistance. However, blending two or more elastomers is not as easy as one would imagine. The work on blending various elastomers conducted by Tinker[28] and coworkers has thrown some light on the importance of compatibility, distribution of crosslinks in each rubber phase, distribution of filler and plasticizer and interfacial tension of each phase which have very strong influence on the service performance of the blend. When the elastomers are not compatible with each other, the associated problems that may arise include maldistribution of crosslinks, partition of chemicals (sulfur, accelerators, etc.) due to mechanism associated with preferential solubility and others. Lewan[29] worked on crosslink density distribution in NR/NBR blend and reported the effects of large difference in polarity and solubility parameters between these two rubbers. The large difference in polarity has the following effects:

(i) causes high interfacial tension that is detrimental to mixing since it interferes with efficient mixing at the interface, hence minimizing the opportunity for crosslinking between the rubbers;
(ii) causes poor phase morphology, which is characterized by large phase sizes;
(iii) causes uneven distribution of crosslinks arises through preferential solubility of the curatives and vulcanization intermediates. Sulfur will be preferentially soluble (partition in favor of) the more polar NBR. One phase is over-crosslinked and the other is lowly crosslinked.

However, Lewan[29] overcame these problems by selecting the correct type of curing system such as semi-EV based on sulfur – TBBS, to obtain an even distribution of crosslinks in each phase and maximizing crosslinking between rubbers at the interface. The use of compatibilizer is highly recommended to enhance the compatibility between rubber phases. Polychloroprene rubber serves as a very good compatibilizer for the NR/NBR blend with just a small quantity (5 pphr) added to the blend. The addition of this compatibilizer reduced phase sizes, gave an even distribution of crosslinks and increased tensile strength.[30] Blends of elastomers provide alternative means of improving both aging resistance and oil resistance.

3.33.12.3 Antidegradants

Chemical antioxidants and antiozonants combat aging by scavenging harmful radicals, absorbing UV light, deactivating catalytic metals like copper, manganese, iron, etc., and decomposing initiating peroxides.[16,17] Two main types of chemical antioxidants and antiozonants are widely used in rubber compounds; they are amines and phenolics. Amine types are more effective and powerful antioxidants than phenolic types. However, the former is staining and the latter is not. Thus, this limits applications of amine types to black and dark colored elastomeric products. Phenolic types are exclusively used for white and bright colored products, especially in electrical wire insulation where colors are useful for identification purposes. Both amines and phenolics provide protection against aging by scavenging the harmful free radicals during the oxidative chain reaction.[16,17] The proposed mechanism[17] by which these two types of antioxidants work is shown in **Figure 18**. During the initiation stage, the free radicals produced by the peroxides abstract a labile hydrogen atom from the antioxidant and produce an antioxidant radical. This antioxidant radical is more stable than the peroxy radical, which terminates by reaction with other radicals in the system.[16,17]

The transfer step (c) and termination step (f) remove the free radical functionality from the elastomer, which consequently halts the oxidative degradation reaction.[17] Metal deactivators such as 2-mercaptobenzimidazole and its salt when added into the rubber compound containing amine or phenolic antioxidant give a synergistic effect to enhance the protection against aging.[31] These chemicals form

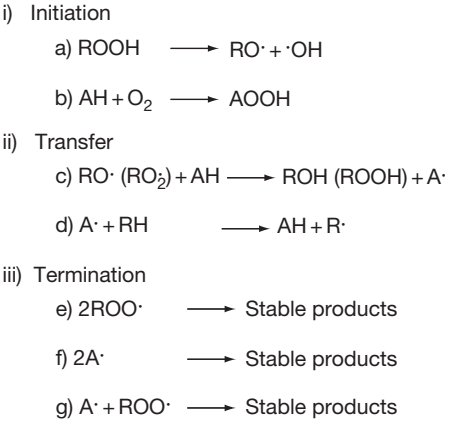
i) Initiation
a) ROOH → RO· + ·OH
b) AH + O2 → AOOH
ii) Transfer
c) RO· (RO2·) + AH → ROH (ROOH) + A·
d) A· + RH → AH + R·
iii) Termination
e) 2ROO· → Stable products
f) 2A· → Stable products
g) A· + ROO· → Stable products

Figure 18 Mechanism of amine and phenolic antioxidant activity, where AH is the antioxidant.[17]

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coordination complexes with catalytic metals and inhibit metal-activated oxidation. Carbon black is a natural UV light absorber, and for nonblack compounds, it is useful to incorporate a UV light absorber such as benztriazole derivative.

3.33.12.3.1 Mechanism of antiozonant action

The mechanism by which an antiozonant protects unsaturated rubber against ozone cracking has received attention from many rubber chemists and physicists. A number of suggestions have been proposed as to how antiozonants confer protection, ranging from competitive reaction with ozone (scavenging) to various types of protective layer formation.[17,19–21] There are three theories to describe the mechanism of antiozonant action[17]:

(i) The antiozonant blooms to the surface of the rubber compound and reacts preferentially with the incident ozone.
(ii) The antiozonant blooms to the surface of the rubber and forms a protective layer of film on the surface.
(iii) The antiozonant reacts with intermediates formed in the ozonation of rubber, preventing chain scission or recombining severed rubber chains.

Lake[32] has conducted some work to elucidate the mechanism of antiozonant action to protect natural rubber against ozone cracking. He used dioctyl-*p*-phenylenediamines (DOPPD) antiozonant for his rubber compound. Exposing the rubber test-piece to ozone-rich atmosphere has reportedly resulted in a layer of film 10^{-3} cm thick and visible to the naked eye forming on the rubber surface.[32] The protective layer can be removed by physical means either by scraping or using adhesive tape, or by swabbing with cotton wool dipped in acetone. The mass of the film can be determined by weighing the test-piece before and after its removal. In this way, the kinetics of layer formation can be determined by monitoring changes in weight after various periods of exposure to ozone.

Lake[32] has derived a mathematical expression to relate the mass of layer per unit area of surface M_L formed after time t to the concentration C_0 of antiozonant in the rubber and diffusion coefficient D_L as shown by eqn [14]:

$$M_L = [2\rho_L D_L S_L C_0 t]^{1/2} \qquad [14]$$

where ρ_L is the density of the layer material and S_L is the solubility, relative to that in the rubber, of the antiozonant in the layer. In deriving this equation, Lake[32] assumed that the layer to be formed entirely of reacted antiozonant and the concentration of unreacted material within it to be small. The product $D_L S_L$ was determined experimentally by measuring the rate of transfer of antiozonant through the layer formed on a test-piece to a controlled rubber test-piece containing no antiozonant initially. This was done experimentally by pressing two cylindrical discs (test-piece A contains antiozonant, test-piece B has no antiozonant) together so their surfaces are in intimate contact with each other. The antiozonant from test-piece A would migrate into test-piece B as a function of time. The mass of the layer formed per unit area of surface was plotted against the square root of time to produce a straight line whose slope gave the value of $M_L/t^{1/2}$, that is mass of film deposited per square root time. Lake[32] obtained very good agreement between theory and experimental data.

Lake[32] proposed the mechanism of antiozonant action as follows: The protective layer formed on the rubber surface is composed predominantly of the antiozonant which has reacted with ozone. The film formed remained essentially in the unstrained state, independent of the type of deformation applied. For this to happen, it is necessary that the antiozonant is soluble in the rubber, and that its reaction product should be insoluble. However, once the protective layer becomes coherent and compact, it will reduce substantially the flux of ozone reaching the rubber surface. Thus it appears that the ability of the antiozonant to prevent cracking is likely to be determined by what occurs during the initial stages of exposure when the layer is starting to form, rather than by the long-term behavior. Indeed, Lake[32] suggested that a coherent monomolecular layer of film that formed on the rubber surface is sufficient to confer protection against ozone cracking. However, the time for this monolayer to form must be faster than the time for the crack to grow to the same depth, so that the monolayer is able to bridge any cracks that have begun to grow.

3.33.12.3.2 Theories of layer formation

The thin layer of protective film covering the rubber surface is a direct consequence of the chemical reaction between chemical antiozonant and ozone. Lake and Mente[21] proposed two diffusion models to work out a theory for layer formation. The two models are shown in **Figure 19**. The first model describes the rate of layer formation that is controlled by the diffusion of the antiozonant across the already-formed layer to react with ozone at its outer surface. Under

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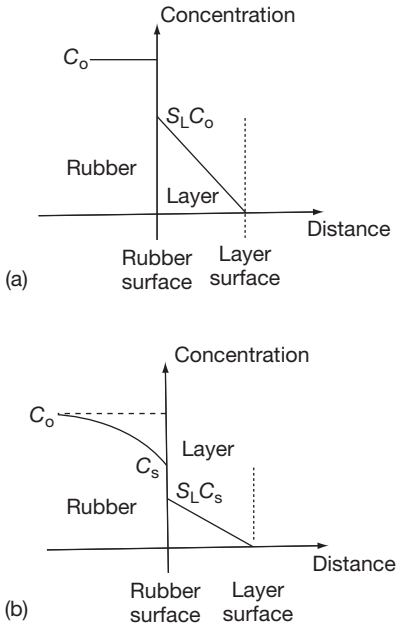

Figure 19 Diffusion models for antiozonant layer formation: (a) rate governed by diffusion of antiozonant within the layer only, and (b) rate governed by both diffusion in the layer and in the rubber. Adapted from Lake, G. J.; Mente, P. G. *J. Nat. Rubb. Res.* **1992**, *7*(1), 1–13, with permission from Malaysian Rubber Board.

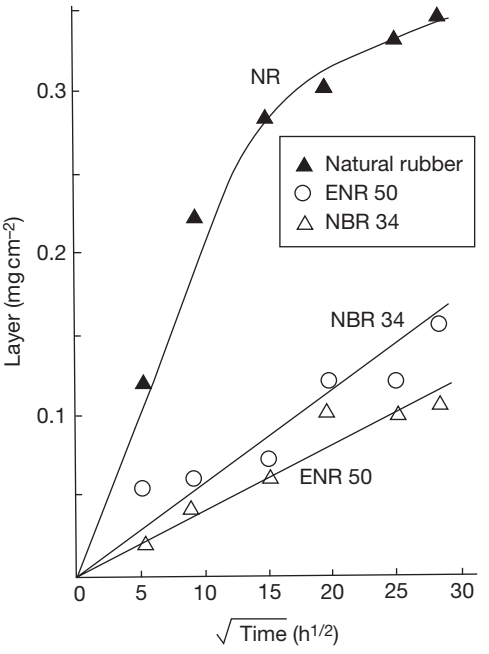

Figure 20 Dependence of the mass of antiozonant layer formed on the square root of the time of exposure to an ozone concentration of 200 pphm at 40 °C for vulcanizates of NR, ENR 50, and NBR 34. Adapted from Lake, G. J.; Mente, P. G. *J. Nat. Rubb. Res.* **1992**, *7*(1), 1–13, with permission from Malaysian Rubber Board.

these circumstances, the mass per unit area M_L, of layer formed after time t is given by eqn [14].[21,32] The concentration gradient in the layer will be essentially linear as shown in **Figure 19(a)**. The second diffusion model takes into account diffusion within the rubber in addition to diffusion across the layer. In this case, an equation similar to eqn [14] applies, when C_0 is replaced by C_s, the concentration at the rubber surface is lower than C_0 as shown schematically in **Figure 19(b)**. C_s is a function of C_0 and the relative permeabilities of the rubber and the layer to the antiozonant, and with the assumptions made, are given by eqn [15]:

$$C_s/C_0 = 1 + \xi - [(1+\xi)^2 - 1]^{1/2} \qquad [15]$$

where

$$\xi = (\pi/4)(\rho_L D_L S_L / DC_0) \qquad [16]$$

and D is the diffusion coefficient of the antiozonant in the rubber. The mass of layer per unit area of surface plotted against square root of time as shown in **Figure 20** enabled Lake and Mente[21] to determine the rates of layer formation of the antiozonants formed on NR, ENR 50, and NBR 34, respectively. These three rubbers differ greatly in terms of polarity and glass-transition temperature, which may affect the rate of film formation on the rubber surface. Their experimental results as shown in **Figure 20** indicate that the rate of layer formation for NR is about four times faster than that of NBR 34 and ENR 50, which is in accordance with the dependence of the diffusion coefficient on the glass-transition temperature of the rubber. The diffusion coefficient decreased in the increasing order of the T_g of the rubber.[21] Thus the diffusion coefficient of NR is fastest and that of ENR 50 is the slowest as T_g of NR is about −69 °C and that of ENR 50 is about −24 °C.[21] NBR34 has a slightly faster diffusion coefficient than ENR 50 as its T_g (−28 °C)[19] is slightly lower than that of ENR 50. Lake and Mente[21] also conducted experiments to investigate the effect of temperature on layer formation on the NR surface at −17 and 23 °C respectively as shown in **Figure 21**. They found that the rates of layer formation at these two temperatures were the same for NR. However, the diffusion coefficient of this particular antiozonant (DOPPD) in NR at −17 °C was very similar to that in ENR 50 and NBR 34 at 23 °C. They attributed this finding to the partitioning of the antiozonant

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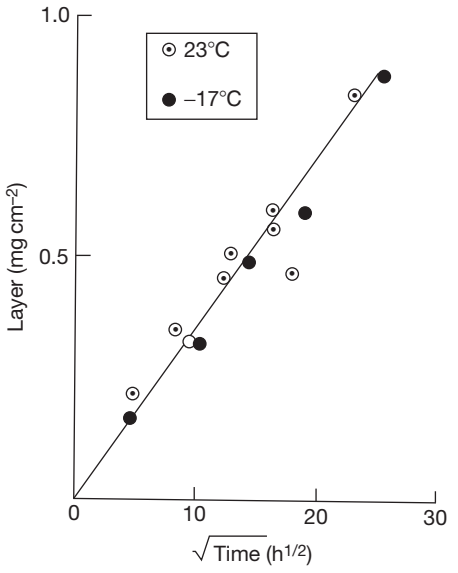

Figure 21 Mass of antiozonant layer formed versus square root of the time of exposure to 10^5 pphm ozone for an NR vulcanizate containing 10 pphr DOPPD at 23 and −17 °C. Adapted from Lake, G. J.; Mente, P. G. *J. Nat. Rubb. Res.* **1992**, *7*(1), 1–13, with permission from Malaysian Rubber Board.

between the elastomer and the layer material, as the polarity of the elastomer affects the solubility of the antiozonant in the rubber. The solubility of the antiozonant varies in the ascending order of polarity of elastomer, that is NR < NBR 34 < ENR 50.[21] Lake and Mente concluded that for elastomers with high T_g, the antiozonant offers better protection at temperatures above room temperature than at low temperature, as the protective agents are more mobile at high temperatures rather than at low temperatures.

3.33.12.4 Blooming of Wax

Besides chemical antiozonants, paraffin wax is also a useful ingredient to confer protection against ozone cracking. Wax provides a protective layer surrounding the surface of the elastomer through the diffusion process commonly known as blooming, which prevents direct contact between ozone and the elastomer. Blooming occurs when the supersaturated solution of the ingredient in the rubber crystallizes more readily on the surface than in the rubber itself.[24,33] This basic mechanism of blooming is not only applicable to wax but other ingredients as well. When other ingredients such as sulfur, accelerators and strearic acid bloom to the rubber surface, they reduce the tackiness of the rubber, which can bring detrimental effects to products relying on adhesion and bond strength involving different components plied together. These include rubber-to-metal bonded components, tires, belts, and hoses. However, blooming of waxes and antioxidants brings advantages.

Nah and Thomas[33] investigated the mechanism and kinetics of diffusion of wax to the rubber surface. They envisaged that the driving force for the blooming process arises from the elastic forces acting around the wax precipitates in the rubber when the wax concentration is in excess of its equilibrium solubility. They then proposed a model and theory for wax blooming base on thermodynamic concept of diffusion, where the driving force of the diffusion process is predominantly associated with free energy gradient rather than the concentration gradient of the wax that is dissolved in the rubber. The initial rate of wax bloom per unit area $(M_t/t^{1/2})$ is given by eqn [17][33]:

$$(M_t/t^{1/2})_{x=0} = [(24 v_f D_t s_x \rho_x V_x G)/RT]^{1/2} (d\lambda/dy)_0 \quad [17]$$

where D_t is diffusion coefficient, v_f is volume fraction of seeding particles or flaws present in the rubber. s_x is solubility of wax in the rubber, ρ_x is density of wax, and V_x is molar volume of solid wax. G is shear modulus of the rubber, R is molar gas constant, T is absolute temperature. $(d\lambda/dy)_0$ is equivalent to the concentration gradient of the wax at the surface of the rubber, and is determined by numerical methods for the appropriate boundary conditions and a suitable value of v_f. The symbol λ stands for the extension ratio of the rubber around the precipitated wax particle, assumed spherical. Nah and Thomas[33] verified eqn [17] experimentally, and obtained satisfactory agreement between their experimental and theoretical values for the migration of paraffin waxes in peroxide cured natural rubber. The theory was applicable to predict the blooming of wax mixtures with success, indicating that the mechanism of wax blooming has been identified correctly. Although Nah and Thomas developed the theory for blooming of wax, with minor adjustments, it is also applicable to predict migration and blooming of sulfur, fatty acids and antidegradants in vulcanized elastomers.

3.33.12.5 Choice of Vulcanization System

Anaerobic aging usually decreases the stiffness, resilience, and tensile, tear and fatigue properties; the extent is mainly determined by the type of vulcanization system, which affects aging of elastomers. There are three types of sulfur vulcanization systems known as conventional, efficient (EV) and

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semi-efficient (semi-EV) respectively[8,10] as discussed briefly in Section 3.33.4.3. The conventional system has a higher sulfur dosage than the accelerator that produces predominantly polysulfidic crosslinks, where the rubber molecular chains are linked by three or more sulfur atoms. Polysulfidic crosslinks have poor resistance to heat aging because the –S–S– bond has low thermal stability. In contrast, EV makes use of the low sulfur level and high accelerator dosage. This EV system produces predominantly monosulfidic crosslinks which are thermally very stable. The rubber network consists of other structural features as described briefly in subsequent sections.

3.33.12.5.1 Sulfur vulcanization system and types of crosslinks on aging resistance

Polysulfidic crosslink

A chain of three or more sulfur atoms (maximum of six atoms) in this crosslink bridges two polymer chains. The bond energy of this crosslink is less than 268 kJ mol^{-1}, which is relatively low.[10] A polysulfidic crosslink can be produced by using the conventional vulcanization system where the quantity of sulfur is more than the quantity of the accelerator in the ratio 5:1 (sulfur: accelerator). Therefore the conventional sulfur cure system is not suitable for high temperature applications.

Disulfidic crosslink

In a disulfidic crosslink, there are two sulfur atoms bridging the two polymer chains. Its bond energy is about 268 kJ mol^{-1}. Little is known of the properties of this crosslink, mainly because it is very difficult to prepare a network in which disulfides are predominant. In both conventional and efficient sulfur vulcanizates the proportion of disulfidic crosslink is seldom more than 20–30% of the total.

Monosulfidic crosslink

In the case of a monosulfidic crosslink, the two polymer chains are bridged by one sulfur atom. Its bond energy[10] is relatively high, about 285 kJ mol^{-1}. A monosulfidic crosslink can be produced from an EV system where the amount of the accelerator is higher than the amount of sulfur, about 5:1 (accelerator:sulfur). Thus the EV system is suitable for medium high temperature applications.

Cyclic sulfides

These are intra-crosslinks which are useless as the crosslinks are formed on the same polymer chain. This phenomenon is also known as main chain modification. The main source of these main chain modifications is the thermal decomposition of polysulfide crosslinks. The conventional vulcanization system creates more cyclic sulfides than the EV system as the former produces more polysufide crosslinks than the latter.

Conjugated diene and triene groups

These main chain modifications are also formed by the thermal decomposition of polysulfide crosslinks. The concentration of these conjugated groups increases on overcure. The presence of these groups tends to catalyze oxidative aging as they are much more susceptible to oxidation than the polyisoprene main chain.[8,10,16]

Pendent accelerator group

It is generally accepted that in accelerated sulfur vulcanization, crosslinks are formed from initial rubber-bound pendent groups in which disulfide or polysulfide chains are terminated by accelerator fragments. Like the crosslink, some of these intermediates undergo progressive desulfuration and are converted into stable monosulfidic links between the polymer chain and accelerator fragments. The extent of main chain modification will depend on the amount of accelerator available and on the ease with which the initial pendent group can be desulfurated.

Extra-network material

The extra-network material formed by a sulfur vulcanizing system can be put into two categories. The first consists of unreacted zinc oxide and fatty acid activators, their zinc soap reaction products and zinc sulfide. The second consists of accelerator reaction products.

3.33.12.5.2 Peroxide vulcanization system

Unlike sulfur vulcanization, peroxide vulcanization does not require the presence of double bonds. In fact, peroxide vulcanization is possible for rubbers having either saturated or/and unsaturated carbon–carbon backbone chains. However, peroxide vulcanization is quite impossible with the following elastomers because of their tendency to decompose:

- IIR – butyl rubber
- CIIR – chlorinated butyl rubber
- CO – polyepichlorohydrin rubber
- ECO – copolymer of epichlorohydrin and ethylene oxide
- PP – polypropylene
- ACM – polyacrylic rubber

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The most common peroxide is dicumyl peroxide (DCP or dicup). Others include ditert butyl peroxide, dibenzoyl peroxide and bis(2,4-dichlorobenzoyl) peroxide. Peroxide vulcanization[10] produces a vulcanizate which will impart good aging resistance and excellent resistance to compression at high temperatures (70–100 °C). To obtain the best compression set performance, freedom from certain other compounding ingredients, especially zinc oxide and stearic acid, is essential. Peroxide vulcanization is essentially nonreverting. However, there are certain deficiencies such as poor hot tear strength and incompatibility with chemical antiozonants. Other technical limitations include slow cure rate with no delayed action, and degradation of the rubber giving a sticky surface if it comes into contact with air during the cure. Thus peroxides are not suitable for hot-air or steam-pan curing. The reaction of peroxide must be carried through to completion to obtain the best heat resistance; therefore long cure times are inevitable. In addition, nearly all antidegradants and aromatic oils affect the efficiency of the peroxide cure.

Co agents, which are highly reactive materials, are usually added in peroxide vulcanization to increase the efficiency of the organic peroxide, but do not affect the rate of cure.[10,31] They are used either to enhance the modulus and hardness or to reduce the level of peroxide required. They can be absolutely essential for the efficient cure of chlorinated polyethylene. Typical solid coagents are zinc diacrylate, zinc dimethacrylate, and *m*-phenylene dimaleimide. Liquid coagents are materials such as triallyl cyanurate (TAC), triallylisosyanurate (TAIC), etc. High vinyl polybutadiene is a polymer which can act as a coagent.

3.33.12.5.3 Vulcanization with urethane

This (urethane) crosslinking system for natural rubber was developed in the early 1980s by the scientists at the Malaysian Rubber Producers Research Association (MRPRA).[10,31] It was marketed under the trademark Novor. The basic reagent is a reaction product of a nitroso compound and a diisocyanate which dissociates at vulcanizing temperatures into its component species. The free nitroso compound then reacts by addition to rubber molecules giving attached pendent groups which subsequently react with the diisocyanate to form urea type crosslinks. The main features of the vulcanizates are excellent reversion resistance and, when protected with a TMQ/ZMBI antioxidant combination, excellent heat aging resistance.

3.33.12.5.4 Metallic oxide vulcanization

Elastomers containing halogens can be cured with metallic oxides such as oxides of zinc, magnesium, and lead. The oxides form an ether type of crosslink (R–O–R′) which gives good heat aging resistance. Elastomers which can be vulcanized metallic oxides are polychloroprene, halogenated butyls, and polychlorosulphunated rubber.

3.33.12.5.5 Resin vulcanization

Resin vulcanization has established itself to some degree in butyl (IIR) crosslinking, giving excellent heat and steam stability.[10] Example of a typical resin cross linker is polymethylolphenolic resin. The amount used is at the level of 5–12 pphr.

3.33.12.5.6 Quinonedioximes vulcanization

p-Benzoquinonedioxime (CDO) as well as its dibenzoyl derivative are cross linkers for many rubbers because of their free radical reactions.[10] Best known and of greatest interest is their use in IIR because of the excellent heat and steam stability that can be obtained. They are used mainly for rubbers having low unsaturation where sulfur vulcanization is slow. They have been unimportant for the classic diene rubbers.

3.33.13 Future Developments in Materials or Applications

Natural rubber and synthetic elastomers are likely to maintain their roles and contributions in domestic and industrial applications, buildings and structures, automotives, and marine and engineering products. With the emergence of nanomaterials for rubber compounding, it is envisaged that future elastomeric products will provide better service and longer life performance than they are capable of providing now. High heat resistant elastomers and highly oil resistant elastomers are the main players of the future to meet the high demands of the automotive industry and aeronautical engineering. More developmental work in these areas is expected.

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